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CONTENTS

AGÓCS, M.: Investigations on the Electrode Potential of Sulfide Ores 61
GRASSELLY, GY.: Correlation Between Electrostatic Energies and Energy Constants of Some Complex Oxyanions 3
GRASSELLY, GY.: On the Phosphorus-bearing Mineral of the Manganese Oxide Deposits of Eplény and Úrkút 73
GRASSELLY, GY. and M. HETÉNYI: Adsorption Properties of Some Manganese Oxides 85
JÁMBOR, Á.: Pleistozene Deflationserscheinungen in südwestlischen Teil des Mecsek-Gebirges 13
MEZŐSI, J.: Contribution to the Knowledge of the Magnetite-Hematite System of Oxyvolcanites 23
MEZŐSI, J.: Potassium Metasomatism in the Neighbourhood of Mátraszentistván (W-Mátra Mountains) 99
MOLNÁR, B.: Lithological and Geological Study of the Pliocene Formations in the Danube-Tisza Interstream Region. Part II 35
MOLNÁR, B.: Tectonic Control of Sedimentation in the Upper Pannonian Section of a Borehole at Macs Great Hungarian Plain, Hungary 109
MOLNÁR, E.: On the Relationship between the Degree of Oxidation of Manganese Oxide-hydrate Precipitates and the Conditions of their Precipitation 121
PÉCSI—DONÁTH, É.: Some Contributions to the Knowledge of Zeolites 127
ROLF SEIM und JÜRGEN EIDAM: Über granitische Verdrängungsgänge im Diorit der Brocken-massiv-Ostrandzone (Harz) 143
VITÁLIS, GY. and J. HEGYI—PAKÓ: Examination of Cement-Industry Raw Materials from the SW Bükk Mountains 47
VITÁLIS, GY. and J. HEGYI—PAKÓ: Geological, Mineralogical and Petrographical Examinations in the Course of Explorations for Binding Raw Materials in the Neighbourhood of Vác . 157

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Kiadványunk címének rövidítése

Acta Miner. Petr., Szeged

CORRELATION BETWEEN ELECTROSTATIC ENERGIES AND ENERGY CONSTANTS OF SOME COMPLEX OXYANIONS

by

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INTRODUCTION

The author in some of his work dealing with the geochemical role and significance of the complex anionic potentials [GRASSELLY, 1959 *a*, *b*, 1960] pointed to that the relative stability relations of the complex anions may be characterized by their electrostatic energy as well by the energy constant (ε_M in kcal) [HUGGINS and SUN, 1946]. The increase of the relative stability of the complex anions is indicated by the increase of the electrostatic energy values computed or by that of the energy constants calculated from thermochemical data experimentally obtained.

In the first step to simplify the problem, the electrostatic energies of the complex anions were calculated on the basis of simple ionic model taking the sum of ionic radii as the shortest distance between cation and anion. Thus, the radius of the O^{2-} anion was taken as 1,32 Å according to GOLDSCHMIDT in the MgO_4^{6-} „complex anion" just as in the ClO_4^{1-} anion only to mention the members of lowest and highest stability, respectively, of the series.

It is clear that this aspect holds good only in first approximation considering the complex anions as ideal formations independent of the crystal lattice, however, the existence of oxygen ions of same character and size in the MgO_4^{6-} complex — which in the lattice of spinel can not be considered as a real complex anion according to MACHATSCHKI [1931] — as well as in the SiO_4^{4-} or in the ClO_4^{1-} complex anion can not be supposed. Still less may be supposed as the bonding character within the complex anions starting from the MgO_4^{6-} toward the ClO_4^{1-} becomes more and more covalent as shown in Table I in the case of some tetrahedral oxyanions.

The increasing covalent character in the series of the complex anions is due to the increasing polarizing force of the central cation. Correspondingly the deformation of the anion increases — in the present that of the oxygen — thus it is not suitable to consider the oxygen ion in each member of the complex anion series with the same character and radius.

Comparing the electrostatic energies calculated from ionic model and the energy constants given by HUGGINS and SUN it seems, however, to be possible to demon-

strate, at least qualitatively, the change in the character of the oxygen and that of the bonding through the series of oxyanions arranged according to their increasing relative stability.

Table I

Complex anion	Difference of electronegativity values of cation and anion	Polarity according to PAULING
MgO_4^{6-}	2,3	73,35%
AlO_4^{5-}	2,0	63,21%
SiO_4^{4-}	1,7	51,44%
PO_4^{3-}	1,4	38,74%
SO_4^{2-}	1,0	22,12%
ClO_4^{1-}	0,5	6,05%

CONSIDERATIONS ABOUT THE POLARIZATIONOF THE OXYGEN IN SILICATES OF DIFFERENT STRUCTURE TYPE

The polarization of the oxygen anion may change even in the same complex anion for example in the silicate anion too as shown by RAMBERG [1952, 1954]. In his assumption the stability of silicates is closely related to the degree of polarization of the oxygen, the more polarized it is the more stable the silicate. RAMBERG pointed out that by increasing number of shared oxygen atoms, i. e. by increasing degree of linkage „...the nonbridging oxygen atoms which surround Fe, Mg, Ca, etc. in olivine and pyroxene have a greater percentage of double-bond character toward the silicon in metasilicates than in orthosilicates." RAMBERG refers to that the electronegativity value of the oxygen increases stepwise from the nesosilicates toward the tectosilicates and due to this fact in the corresponding compounds the bonding character between oxygen of the silicate anion and the neighbouring cations becomes more ionic.

RAMBERG's above-mentioned statements are supported by the examinations of HUGGINS and SUN [1946] and KELLER [1954], respectively, pointing out the change of the energy constant of Si^{4+} (ε_{Si}) in silicates of different structure-type. Similar change may be supposed in the case of the PO_4^{3-} anion too and presumably the value of energy constant of the central cation of each complex anion ready for polymerization changes.

RAMBERG's and KELLER's assumptions concerning the probable change in the electronegativity and polarization of oxygen atoms and the values of energy constants of central cation of oxyanions, respectively, form the starting point of the following consideration.

CORRELATION BETWEEN ELECTROSTATIC ENERGIES AND ENERGY CONSTANTS

As it was mentioned the relative stability of tetrahedral oxyanions could be characterized by the electrostatic energy values calculated in first approximation on the basis of ionic model. The values were calculated from the following equation:

$$U_p = -\frac{4(z_c \cdot z_a - s_p \cdot z_a^2)}{(r_c + r_a)},$$

where z_c and z_a mean the charges of the cation and anion, respectively, r_c and r_a are the radii of the cation and anion, whereas s_p is the screening factor taking into consideration the type of arrangement of the simple anions and 4 is the co-ordination number being tetrahedral oxyanions in question. The numerical value of s_p is 0,92 at the tetrahedral co-ordination. The higher the numerical value of the electrostatic energy expressed in arbitrary units the more stable the oxyanion. The electrostatic energy values were calculated from ionic model only the attractive and repulsive Coulomb-forces, respectively, supposed to be prevalent between opposite and identical charged ions, respectively.

On the other hand, to characterize the relative stability series of the oxyanions the energy constants ε_M computed by HUGGINS and SUN were also used. Although they refer essentially to the central cation, it seemed, however, still possible to take these values as a measure of the relative stability of the different tetrahedral oxyanions.

Each energy constant „...is a measure of the decrease in energy when one g-atom of the ion M and the equivalent number of oxygen ions (O^{2-}) are transferred from the gaseous state to an average simple or complex oxide in the solid state in which each M has as near neighbours only oxygens and each oxygen has as near neighbours only more electropositive atoms." These energy constants depend primarily upon the charge of ions, the interatomic distance between cation and anion, on the co-ordination number — among other factors — as has been stated by HUGGINS and SUN. The higher the numerical value of the energy constant the greater the energy released.

The mentioned authors have pointed out that the attraction between cation and surrounding oxygen contributes most of the ionic energy of formation of a solid compound and though this attractive energy changes from compound to compound, however, not too considerably. According to HUGGINS and SUN the energy of formation (E_i) may be additively computed from the energy contributions originated from the attraction between the positive components and their opposite charged neighbours. So

$$E_i = \sum_M m_M \cdot \varepsilon_M$$

where m_M is the relative number of the metal atoms, ε_M is the energy constant characteristic of the element M deduced from experimentally determined E_i values.

In the author's former papers the correlation between the two values mentioned above and the complex anionic potentials introduced by SZÁDECZKY-KARDOSS [1954] were discussed, the aim of the present paper is to compare the electrostatic energies and the energy constants of the oxyanions.

*

In the values of the electrostatic energy the conditions really prevalent in the crystal lattice concerning especially the bonding character and its change, respectively, are not expressed, as, using simple ionic model, merely the Coulomb-force have been taken into consideration.

On the contrary, the energy constants computed from thermochemical data, i. e. from energy of formations experimentally obtained, probably better approach and represent the circumstances in fact existing in the lattice. The change of these energy constants presumably expresses implicitely the change of the polarizing force of the central cation and as a result, the increasing deformation of the anion, the rate of polarization of the anion and thus the change of the bonding character within the oxyanion too. It is to mention, however, that these energy constants

Table II

Complex anion	r_c	r_c+r_O	U_p	ε_M kcal.	U'_p	r'_O	x_M electro-negativity of the central cation
		calculated from ionic model			given from the diagram of *Fig. 1.*		
MgO_4^{6-}	0,62Å	1,94Å	0,65	912	the same as U_p	1,32 Å	1,2
BeO_4^{6-}	0,33	1,65	0,77	1141			1,5
GaO_4^{5-}	0,58	1,90	4,88	1827			1,6
AlO_4^{5-}	0,48	1,80	5,15	1878			1,5
BO_4^{5-}	0,22	1,54	6,02	2047			2,0
ZrO_4^{4-}	0,74	2,06	8,38	2637	9,40	1,09	1,4
SnO_4^{4-}	0,67	1,99	8,68	2769	10,0	1,05	1,8
TiO_4^{4-}	0,64	1,96	8,81	2882	10,75	0,96	1,6
GeO_4^{4-}	0,50	1,82	9,49	3055	11,65	0,98	1,7
SiO_4^{4-}	0,39	1,71	10,10	3129	12,10	1,03	1,8
SbO_4^{3-}	0,58	1,90	13,30	4250	18,10	0,81	2,1
AsO_4^{3-}	0,43	1,75	14,44	4507	19,55	0,86	2,2
PO_4^{3-}	0,33	1,65	15,32	4737	20,85	0,88	2,1
TeO_4^{2-}	0,53	1,85	17,98	6167	28,50	0,63	2,1
SeO_4^{2-}	0,39	1,71	19,46	6886	32,35	0,63	2,4
SO_4^{2-}	0,28	1,60	20,80	7195	34,05	0,69	2,5
ClO_4^{1-}	0,25	1,57	26,29	9948	49,00	0,59	3,0

The r_c values are the cation radii given by AHRENS and the r_O is 1,32 Å according to GOLDSCHMIDT

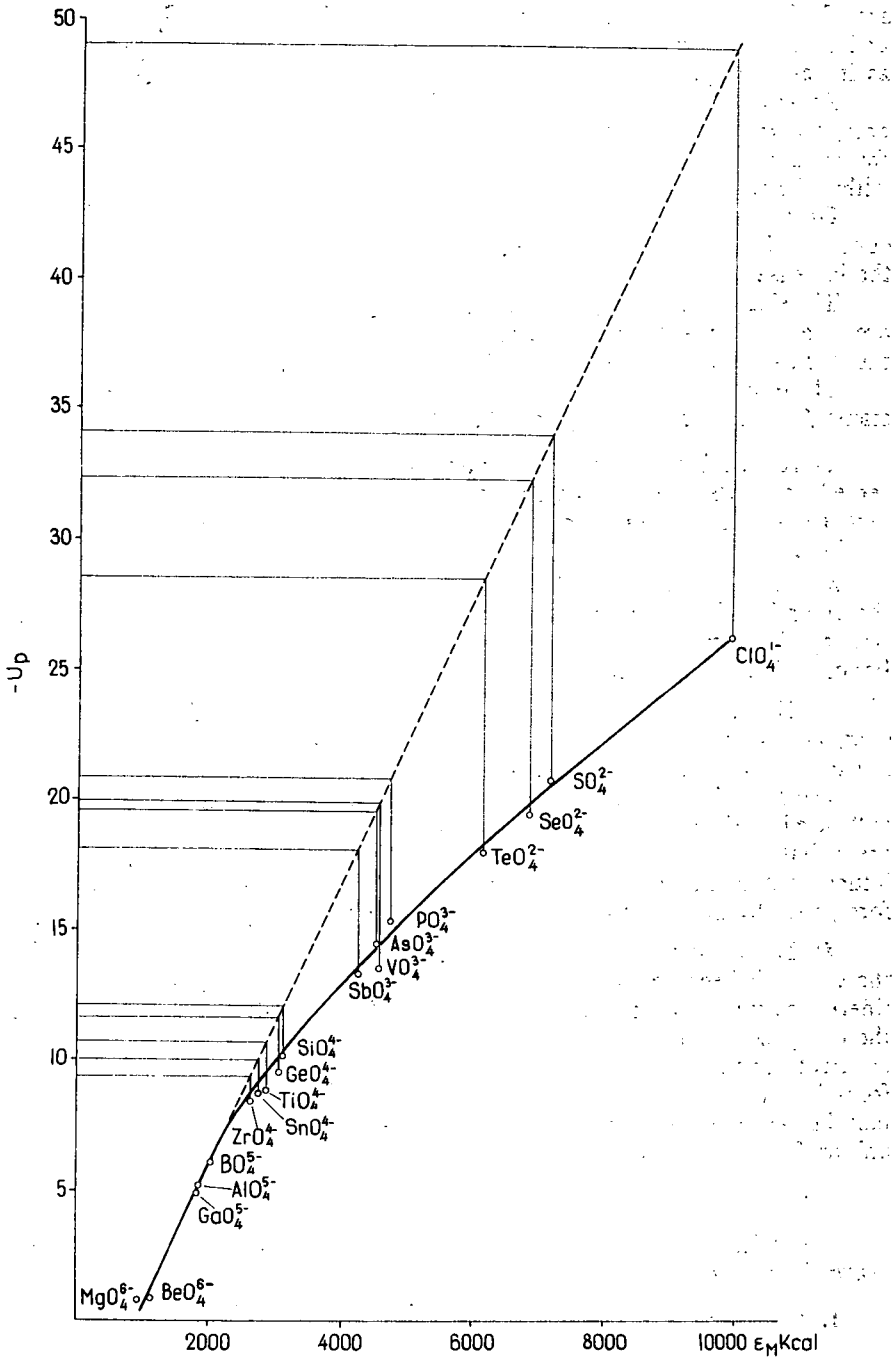

Fig. 1. Correlation of electrostatic energy values and energy contants of tetrahedral oxyanions.

are of adequate precision only for an approximation as they are only average values and „...they do not give accurate energies of formation by simple additivity..." as it has been pointed out by the authors.

At any rate, one of our starting points is the obvious fact that the electrostatic energy computed simply from ionic model can not characterize the oxyanions in the solid crystal lattice all the less the more covalent bonding character prevails within the complex anion, i. e. the greater is the deviation from the pure ionic model.

On the other hand — and this may be our second starting point — the energy constants implicitely express the increasing polarization of the oxygen as well as the increase of the covalent bonding character in this series.

The electrostatic energies and energy constants concerning tetrahedral oxyanions are comprised in Table II. *Fig. 1* shows the electrostatic energy values plotted against the corresponding energy constants.

Plotting the electrostatic energy values against the corresponding energy constants *(Fig. 1)* the following may be established.

a) As the increasing electrostatic energies and energy constants, respectively, served as a measure for the increasing stability of the complex anions, they are arranged in the diagram from left to right upwards corresponding to their increasing stability.

b) Considering the series as a whole, the increase of the electronegativity of the central cation goes nearly together with the increase of the stability as shown also by the data of Table II. This also denotes the gradual decrease of the ionic bonding character in the series.

c) The correlation between the values of electrostatic energies U_p and the energy constants ε_M in the field of anions of lower stability seems to be approximately linear apart from scattering of the points due to inaccurate data.

The linearity may be interpreted that the bonding in these complexes are still dominantly of ionic character thus the U_p values computed from ionic model are suitable to characterize the relationship within the complex anions in solid lattices just as the energy constants calculated from experimental data taking therefore generally better into account the actual relationship of the oxyanions.

d) The deviation from the linearity begins about at the ZrO_4^{4-} and toward the ClO_4^{1-} it becomes more and more pregnant. Should the energy constants considered suitable to characterize with a good approximation the relation within the complex anions, the greater the deviation from the linearity, due to increasing covalent bonding character, the less are able the electrostatic energy values computed from ionic model to characterize the actual situation. The rate of the deviation may be taken as a qualitative measure of the deviation of the real state of complex anions from the ionic model.

*

The following considerations may be further added to the establishments drawn from *Fig.* 1.

1. *Correction of the electrostatic energies computed*

Calculating the electrostatic energies the covalent bonding character, the deformation of the oxygen atom depending upon — among others — the polarizing force of the central cation were not taken into consideration. Should it have been

done by some appropriate way (as for example is given in RAMBERG's work referred), the electrostatic energy would have a greater numerical value denoting the increase of the stability, the increase of the covalent character. In this case the correlation of electrostatic energies and energy constants — apart from some scattering — would be probably linear within the whole series.

It seems that from the correlation plotted — without calculations — at least with approximate accuracy such electrostatic energy values could be obtained in which also the increasing covalent bonding character would implicitely expressed and so they can characterize the complex anions as elements of solid crystal lattices too.

Let us lengthen the lower linear part of the diagram of *Fig.* 1 and draw vertical lines from the points corresponding to the different oxyanions till to the intersection of this lengthened straight line and then project these points of intersection to the U_p axis. The values (U'_p) obtained in this manner are greater than the calculated U_p values as shown in Table II and these U'_p values may be considered as the more probable values for electrostatic energies of oxyanions.

2. *The transition from ionic oxygen radius to covalent oxygen radius in the series of* MgO_4^{6-}-AlO_4^{5-}-SiO_4^{4-}-PO_4^{3-}-SO_4^{2-}-ClO_4^{1-} *anions.*

From the afore-mentioned correlation may be possible to draw some conclusions concerning the radius of the oxygen in the different oxyanions. It may not be supposed the existence of oxygen atoms of the same size and character in the MgO_4^{6-} complex and in the SO_4^{2-} or in the ClO_4^{1-} anion. The polarity of these anions see in Table I. Should the PAULING's electronegativity values and their differences, respectively, well characterize the ionic percentage of the bonding, in the MgO_4^{6-} complex we can reckon with the real oxygen ion and with its ionic radius, however, in the case of SO_4^{2-} or even in the ClO_4^{1-} anion — in the bonding of the latter already 94% covalent character prevails — we should rather suppose oxygen atom and calculate with the corresponding radius value. It seems that from the rate of deviation from the linearity conclusions may be drawn concerning the rate of the change of the oxygen radius.

In the series of MgO_4^{6-}-AlO_4^{5-}-SiO_4^{4-}-PO_4^{3-}-SO_4^{2-}-ClO_4^{1-} in first rough approximation the charge of cation and anion, the tetrahedral co-ordination and presumably the radius of the central cation may be considered as unvariable and as the lone variable the radius of the oxygen can be taken.

Substituting the U'_p values for the equation of the electrostatic energy and taken as unknown in the equation only the radius of the oxygen, the latter may be calculated (Table II).

As in the sequence of oxyanions $SiO_4^{4-} \rightarrow ClO_4^{1-}$ the bonding character between the central cation and the oxygen becomes more and more covalent, the radius of the oxygen also approaches the covalent oxygen radius. It may be said that the oxygen radii computed in the way outlined above may be considered as transitional oxygen radii corresponding to the ratio of ionic — covalent character prevalent in the given complex anion if the oxygen would be hypothetically taken as spherosymmetrical.

The fact that by increasing covalent bonding character the features of the oxygen atom become dominant instead of that of the oxygen ion, may be demonstrated also by the change of the size of the oxygen. Plotting the oxygen radius

obtained for the complex anions mentioned against the corresponding differences of electronegativity values of central cation and oxygen, the correlation shown by *Fig.* 2 can be seen.

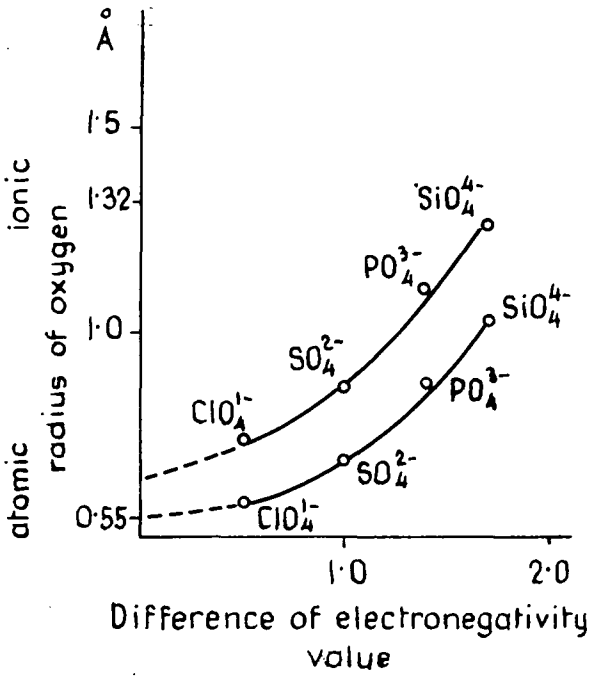

Fig. 2. Correlation of electronegativity differences of cation and anion and the radius of oxygen graphically determined and computed from the diagram of *Fig. 1.*

Fig. 2 shows two curves. The curve 1 is obtained taking into consideration as transitional oxygen radii the following values in the different complex anions:

SiO_4^{4-}	$r_0 = 1{,}27$ Å	SO_4^{2-}	$r_0 = 0{,}87$ Å
PO_4^{3-}	$r_0 = 1{,}11$	ClO_4^{1-}	$r_0 = 0{,}74$.

These values are obtained if at the plotting of the diagram of *Fig* 1 the calculation of the electrostatic energies is carried out using the cation radii of AHRENS and the oxygen anion radius of PAULING (1,40 Å). The curve 2 is obtained on using the cation radii of AHRENS and the oxygen anion radius of GOLDSCHMIDT (1,32 Å) at the calculation the U_p values. In this latter case the transitional oxygen radii computed from the U'_p values are as follows:

SiO_4^{4-}	$r_0 = 1{,}03$ Å	SO_4^{2-}	$r_0 = 0{,}69$ Å
PO_4^{3-}	$r_0 = 0{,}88$	ClO_4^{1-}	$r_0 = 0{,}59$.

As the difference of the electronegativity values decreases the bonding within the complex anion becomes more covalent. Extrapolating the curve 1 the radius of the oxygen will be about 0,64 Å which is very close to the single-bond atomic

oxygen radius (according to PAULING 0,66 Å), whereas the extrapolation of the curve 2 results in an oxygen radius of 0,55—0,56 Å, nearly the oxygen atomic radius of double—bond character (according to PAULING 0,55 Å).

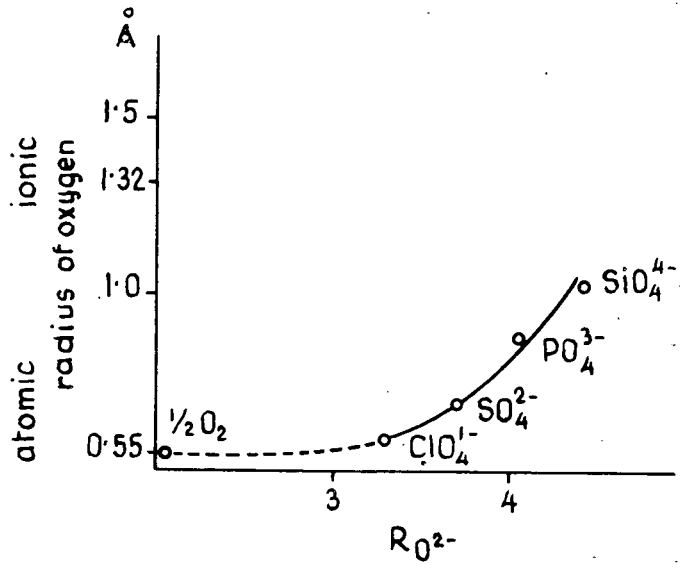

Fig. 3. Correlation of oxygen radius computed and the refraction of oxygen.

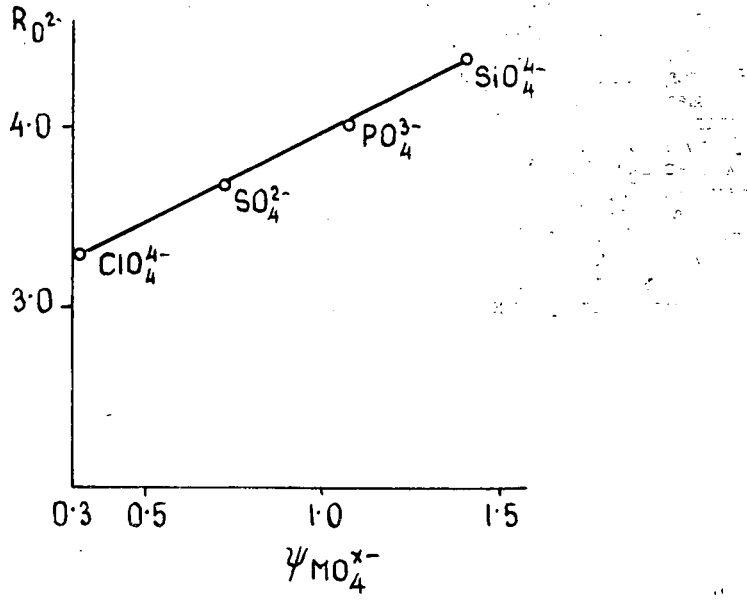

Fig. 4. Correlation of complex anionic potential and the refraction of oxygen.

Similar picture can be obtained plotting the oxygen radius values computed against the refraction values of oxygen (R_0^{2-}) as seen in *Fig.* 3. It was shown by FAJANS that the greater the polarizing force of the central cation the greater extent will be deformed the electron shell of the anion, the lower will be the anion refraction. For example the refraction values in some oxyanions are as follows:

Complex anion:	SiO_4^{4-}	PO_4^{3-}	SO_4^{2-}	ClO_4^{1-}
R_0^{2-}	4,42	4,05	3,70	3,30

whereas the refraction of the non-polar bound oxygen is 2,02. As it is seen by extrapolating the curve, the oxygen radius of double-bond character is approached again.

Finally is worth to mention the correlation of the oxygen refractions and the complex anionic potentials of the corresponding complex anions as shown in *Fig* 4. The correlation is linear between these two values in this series of anions. This may be considered as a further verification that the complex anionic potentials introduced by SZÁDECZKY-KARDOSS are able to geochemical characterization of complex anions in the most different aspects and on the other hand, this correlation shows that the geochemical potential concept furnishes wide usable connections between geochemical and crystallo-chemical problems.

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PLEISTOZÄNE DEFLATIONSERSCHEINUNGEN IM SÜDWESTLICHEN TEIL DES MECSEK-GEBIRGES

von

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In der Zeit des Pleistozäns stellte das Karpat-Becken ein periglaziales Gebiet dar. Dementsprechend wurde es durch fluviale und äolische Ablagerungen und durch Gehängeschutt-Anhäufungen charakterisiert. Die Flugsand- und Lössbildung wurde an vielen Stellen durch gutgebildete Deflationsformen begleitet.

Im Mecsek-Gebirge waren bisher nur Löss und fluviale Ablagerungen als pleistozäne Bildungen bekannt. M. PÉCSI hatte die über der Ortschaft Kővágószöllős sich erhebenden „Babás" Steinbildungen in seinen Universitäts-Vorlesungen (1953) als charakteristische, windgeformte Felsen gemeint. Unsere eigene Untersuchungen haben auch bestätigt, dass in der Entstehung der auf verhältnismässig weicheren, mittelpermischen Schichten entstandenen Becken von Kővágószöllős und Cserkút hauptsächlich die Deflationstätigkeit eine Rolle gespielt hatte. Nach Südwesten von Cserkút erwähnt E. VADÁSZ [1963] ein Stück eines, wahrscheinlich durch den Wind der pleistozäner Zeit glatt-abgenutzten verkieselten Baumstammes. Den ersten unmittelbaren Beweis für die pleistozäne Deflationstätigkeit haben wir im Profil eines, auf der östlichen Seite der Zufahrstrasse von Kővágószöllős abgetäuften Wasserleitungs-Grabens, in dem Mecsek-Gebirge gefunden *(Abb.1* und *2)*. Die Lage des erwähnten Profil-Teiles zeigt in seinen Zusammenhängen die *Abb. 3*. Im Wasserleitungs-Graben wurden die permischen Schichten nur an einigen Stellen erreicht. Diese sind entweder durch ihre eigenen, an der Stelle zurückgebliebenen Verwitterungsprodukte oder (wie das die *Abb. 3* zeigt) durch Bachseife bedeckt. Diese letzte besteht aus schlechtsortiertem, gelbbraunem, stellenweise quergeschichtetem schottrigem Sand. Seine Kiese stammen entweder aus der Umhäufung der Schotter des permischen Konglomerats, oder aus der Denudation der permischen Sandsteine. Diese letzten sind schlecht abgerundet, nur sind ihre Kanten und Ecken rund. Die permischen Schotter bestehen zum überwiegenden Teil aus Quarz und Quarzporphyr. Nach E. NAGY [1959] und auf Grund unserer eigenen Untersuchungen sind sie mittelmässig abgerundet. Die permische Herkunft der Schotter des Konglomerats und des Sandsteines von Jakabhegy kann man auch nach mehrmaligen Umhäufungen feststellen, auf Grund ihrer lilafarbigen, durch den die Haarrise ausfüllenden Hämatit hervorgerufenen Verfärbung. Ein Teil der in der Bildung No 2 des Grabens sich befindenden Schotter stammt auch aus dem Konglomerat von Jakabhegy. Unter diesen (s. Tafeln) konnten wir zwei Stücke finden, die charakteristsche, windgeformte, matt abgenutzte Flächen haben. Auf

den Dreikanter-Kiesen der *Abb. 5, 8* und *9* des Tafels II. kann man auch einen Teil der Oberfläche der fluvialen Bearbeitung beobachten. Zweie von diesen sieben Stücken stammen aus der frischen Erdaufschüttung des Grabens, und fünf aus dem auf der Seite des Grabens anstehenden schottrigen Sand. Das Material aller sieben

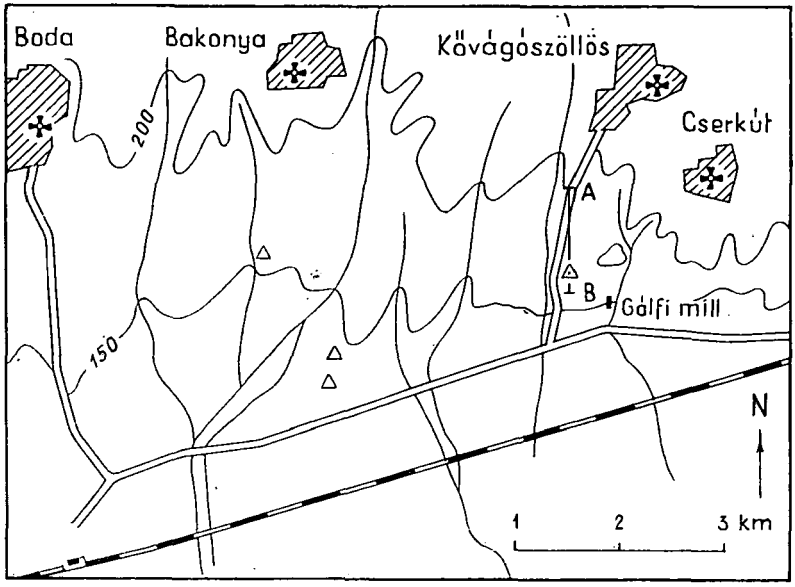


Abb. 1. Situationsskizze der Dreikanter-Lager des Mecsek-Gebirges (nach der Touristenkarte, 1958). (Der lehre Dreieck weist auf die Oberfläche-Vorkommen, der volle Dreieck auf die im Wasserleitungsgraben gefundenen Dreikanter-Vorkommen. A—B: Die Richtung des in der Abb. 3. dargestellten Profils.

Dreikanter-Kiesel stimmt mit denen des Jakabhegyer Konglomerats überein. Mit ihrem Charakter liefern sie aber ein ausgezeichnetes Beweis für eine dauernde und wirksame Windtätigkeit.

Die Tatsache, dass die Bearbeitung der Kiese der würmischen Lössbildung vorausging, ist zweifellos, da würmische Lösse auf der höchsten Schicht dieser letzten lagern. Nach L. MOLDVAY [1964] ist dieser Löss dennoch nicht von unmittelbarer äolischer Herkunft, sondern ist er eine auf der ursprünglichen Stelle gebliebene, durch Bodenfluss umgehäufte, nur in der glazialen Zeit entstandene Bildung. Die letzte Schicht ist dagegen keine äolische Bildung; auf ihren Sandkörnern kann man die Spuren der Windtätigkeit nicht sicher feststellen. Ihre Querschichtung, die orientierte Lage der Schotter-Hauptflächen, die limonitische und kalzitische Inkrustierung der Kiese und ihre Ähnlichkeit den in den würmischen Löss eingelagerten schottrigen Sanden (Schicht No. 4) ferner ihre Terrainlage sprechen alle für das pleistozäne Alter dieser Schicht. Der Neigungswinkel der Querschichten und der Schotter-Hauptflächen sind ein Beweis für einen Wasserstrom von NO nach SW. (Der Neigungswinkel der Querschichten ist zwischen 210—215°). Dieser Schotter kam (beisammen mit dem über dem Löss gelagerten) aus der Richtung der Ortschaft Kővágószöllős und hatte (mangels eines Engpasses bei der Mühle Gálfi) durch seine hiesige SW-Kurve das sich von der Mühle nach N befindende Hügelchen

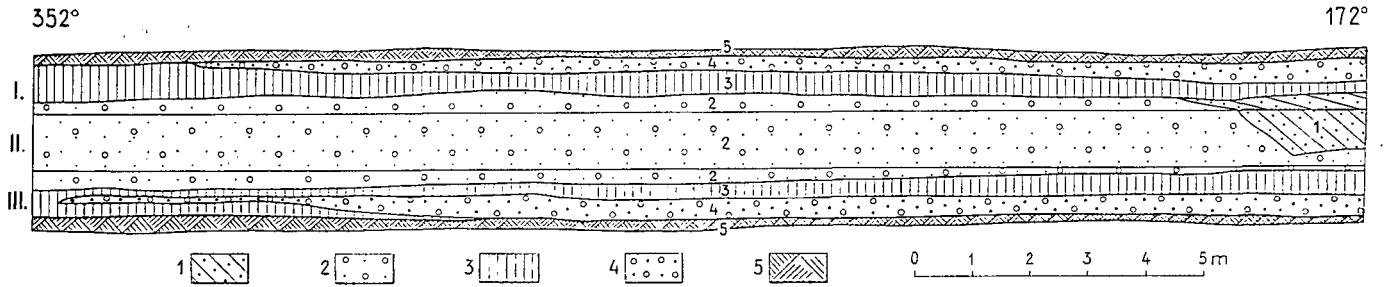


Abb. 2. Das Profil des Wasserleitungsgrabens von Kővágószőllős. *1.* Roter Sandstein mit kieseligem Zement (Perm); *2.* Rotbrauner, schottriger Sand (Riss-Würm); *3.* Gelber Löss (Würm); *4.* Rotbrauner, schottriger Sand (Würm); *5.* Boden (Holozän).

(+200 m Meereshöhe), umgegangen. Das heisst, die Bergrand-Teile der für die permischen Gebiete des westlichen Mecseks so charakteristischen steilen Quertale wurden nur nach den infolge der jüngeren Bewegungen entstandenen postwürmischen Erhebungen gebildet [P. Z. SZABÓ, 1955 und 1957; L. MOLDVAY, 1964*a* und *b*].

Die Dreikanter-Kiesel sind demnach an der Oberfläche des Gehängeschuttes der Umgebung von Kővágószöllős entstanden, und sie sind von hier mit dem Wasser des Baches, in einem späteren Zeitpunkt auf ihre jetzige Stelle gerieten. Eine Voraussetzung ihrer permischen Bildung kann dadurch weggeräumt werden, dass 1*)* Die fluviale Bildung des Jakabhegyer Konglomerats ist zweifellos; 2*)* Trotz den vielen tausenden Aufschlüssen und Dünnschliffe wurden bisher keine windbearbeiteten Sandkörner und Kiese in der permischen Schichten des Mecsek-

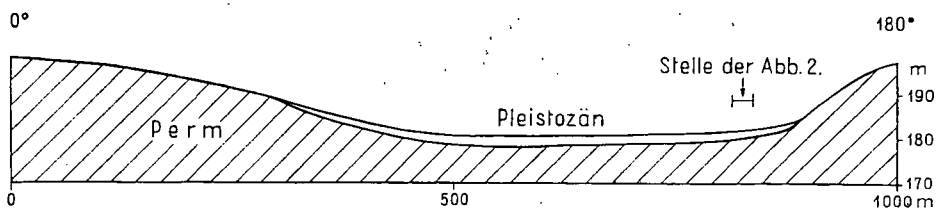


Abb. 3. Prinzipielles Profil längs des Wasserleitungsgrabens von Kővágószöllős. Das Pleistozän besteht im höheren Niveau (links) aus Löss; im tieferen (in der Mitte und rechts) aus Löss und Bachschutt.

Gebirges gefunden. Doch kann die Frage sich stellen, dass ihre Bearbeitung vor der helvetischen oder oberpannonischen Umhäufung stattgefunden hatte. Das ist dennoch — infolge des für das Mecseker Miozän und Pannon festgestellten tropischen bzw. subtropischen Klima — ausgeschlossen. Auf diesem Grund kann das Alter unserer Dreikanter-Kiesel nur als pleistozän festgestellt werden, wie das auch in den anderen Fundorten unseres Landes bestimmt wurde [K. PAPP, 1899; Z. SCHRÉTER, 1910; L. LÓCZY, senior, 1913; F. SCHAFARZIK—A. VENDL, 1929; S. JASKÓ, 1937; E. VADÁSZ, 1953; M. PÉCSI, 1959. s. *Abb. 4*]. Nach dem pleistozänen Grundprofil von Paks [P. KRIVÁN, 1955] ist im Interglaziale Mindel—Riss, im unteren Teil des oberen Risses und an der Grenze Riss—Würm eine, durch die westlichen Winde aufgebaute bedeutende Flugsandbildung nachweisbar. In der Umgebung des Mecsek-Gebirges, auf der südlichen Seite des Kapos—Tals hatten die nordwestlich-südöstlichen Winde pleistozäne Flugsandbildungen gebildet [I. MIHÁLTZ, 1952]. Aus dem Dreiecke der Flüsse Drau—Donau erwähnt GY. PEJA [1955] rotgefärbte Flugsand—Dünen. Er, betont, dass ihre Farbe von dieser der Flugsande des linken Ufers der Donau in der Strecke Vác—Mohács, different ist. Unserer Meinung nach, ist das nicht mit dem farbenden Einfluss der roten pleistozänen Tone verbunden, sondern damit, dass das Material der fraglichen Dünen aus dem Umwehen des frostverwitterten Schuttes der roten permischen Sandsteinschichten stammte. Von der südlichen Seite des Villányi-Gebirges erwähnt L. STRAUSZ [1952] windangehäufte Sande; diese stammen aber warscheinlich aus dem Hochwassergelände der Drau, und sind sie nach P. Z. SZABÓ [1957] altholozänen Alters. Ebenso erwähnt L. STRAUSZ [1952] einen pleistozänen, fluvialen, schottrigen Sand auf der südlichen Seite der Erhöhung, die sich nach Norden vom Villányi-Gebirge befindet. Ihre permische Herkunft wurde zuerst von P. Z. SZABÓ erkannt [1955], später haben auch wir das festgestellt, in Zusammenhang mit der Untersuchung

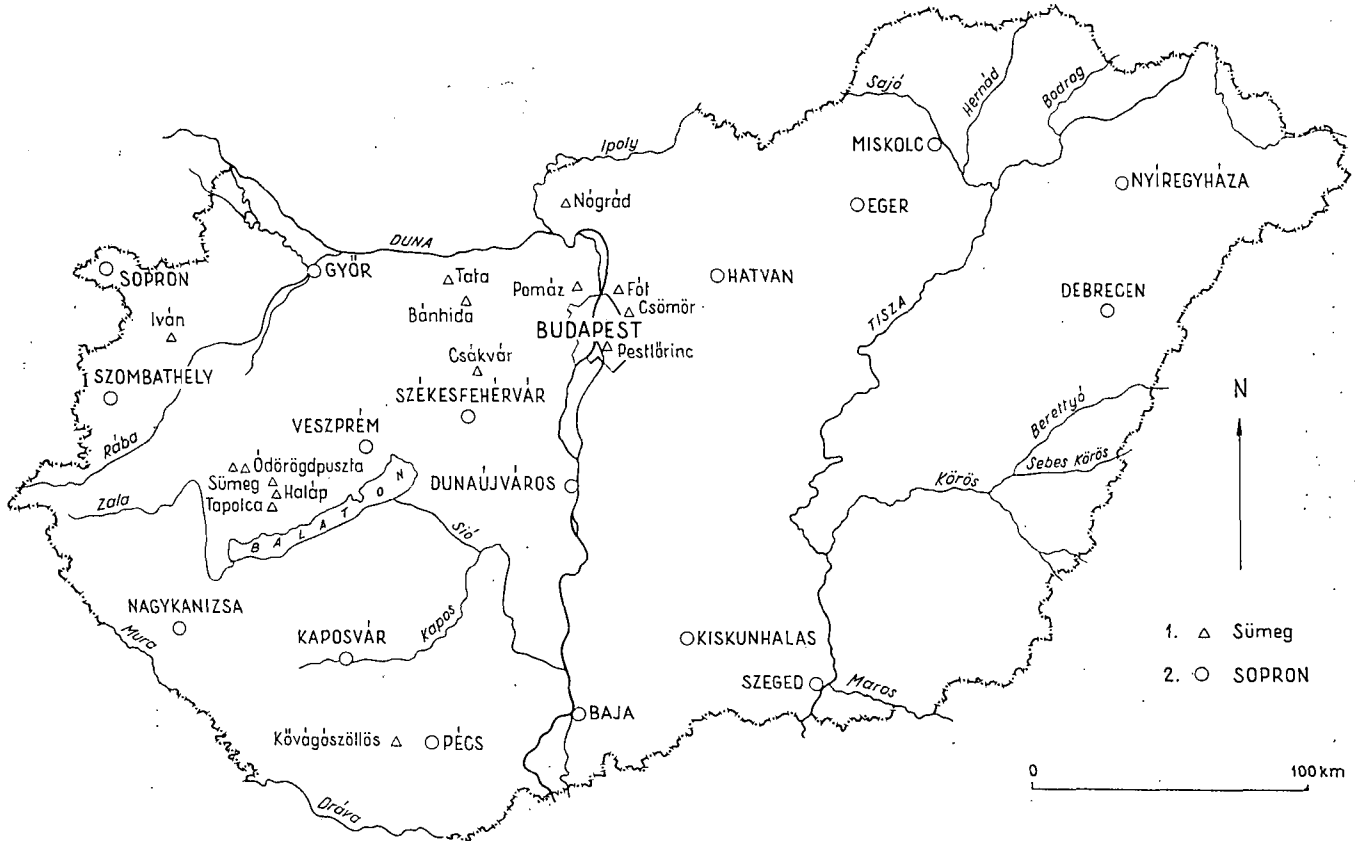


Abb. 4. Quartäre Dreikanter-Kiese in Ungarn.

1. Die Bezeichnung der Fundorten.
2. Grössere Ortschaften.

der Bohrung Gyód, No 4. In dieser Bohrung haben wir im Liegenden des 25 m mächtigen, gelben, würmischen Lösses (zwischen 0—39 m) einen braunen, mittelkörnigen viele windgewehte Körner enthaltenden Sand gefunden, unter dem, bis zur Tiefe 57 m — im Hängenden des hellgelben und grauen oberpannonischen Schichtkomplexes — ein homogener, roter, äolischer Ton folgte. Diesen, dem Aussehen nach, den Materialen der Schichten No 2 der *Abb. 2* ähnlichen Sand hält P. Z. SZABÓ für fluviale Ablagerung. Auf Grund der abgerundeten Körner können wir ihn eher für äolisch halten.

Die ganz abgerundeten Sandkörner mit einem Durchmesser von 0,5—1,5 mm, die wir nach Norden von Mecsekszentkút am Gipfel des Vöröshegy, im roten äolischen, dem würmischen Löss älteren Tone, in einer Menge von einigen Prozenten finden, weisen ebenso auf eine bedeutende Windtätigkeit.

Die obengenannten Bildungen können wir in die folgende genetische Einheit zusammenfassen:

Die dem Würm vorhergehenden Lössbildungen wurden im westlichen Teil des Mecsek-Gebirges in der Zeit des Interglazialen Riss—Würm zum überwiegenden Teil erodiert, ihr kleinerer Teil ist in roten Ton umgewandelt. Nach der Bildung roter Tone haben die starken NW—SO Winde den feinkörnigen Teil des in der Zeit des trockenen und kalten Klimas angehäuften Schuttmaterials — in der Gestalt von Flugsand — auch weit über den Görcsöny-Zug weggetragen. Ein Teil der zurückgebliebenen grösseren Stücke des in der südlichen Hälfte der Mecseker permischen Antiklinale früher angehäuften Gehängeschuttes zeigt characteristische windbearbeitete Flächen. Diese befinden sich schon nicht an ihrer urspünglichen Stelle, sondern sind sie durch die Tätigkeit der der Würmischen Lössbildung vorhergehenden Bächlein umgehäuft. Ihr Alter kann im Zeitraum des Pleistozäns nicht genauer festgestellt werden.

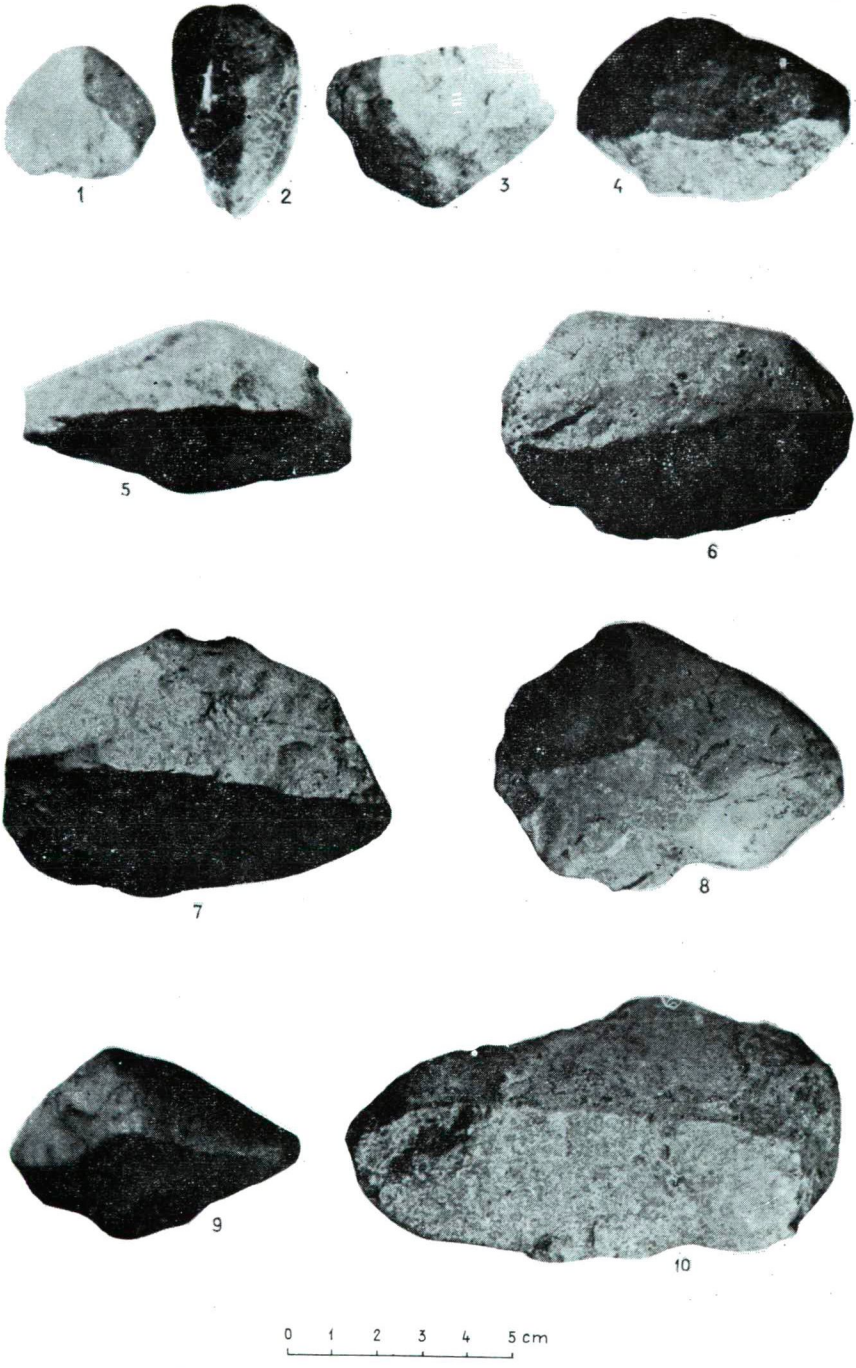
Zur besseren Übersichtlichkeit habe ich auf Grund literarischer Angaben die Karte der ungarischen Fundorten der quartären Dreikanter-Kiesel zusammengestellt. Dreikanter-Kiesel treten in der Zone auf, wo die quartären, wilden, nordwestlichen Winde ihren Flugsand ganz frei über die gröberes Schuttmaterial enthaltenden Oberflächen-Ablagerungen — hauptsätzlich über die Gehängeschütte — herumschleppen konnten. Es ist auffallend, dass wir auch keinen Dreikanter nördlich vom Cserhát-Gebirge und im südwestlichen Teil Ungarns, auf den gröbere Schuttmateriale liefernden Gebieten finden, oder diese mindestens seltener auffindbar sind — im Zusammenhang damit, dass das Ostrowski-Gebirge, bzw. die Alpen die Auswirkung der nordwestlichen, trockenen Winde gebrochen haben.

TAFELERKLÄRUNGEN

TAFEL I

Die besser entwickelte Fläche der Dreikanter-Kiesel.

1.	Dreikantiger Quarzporphyrkiesel	Gesammelt von: JÁMBOR, Á.
2.	Dreikantiger metamorpher Quarzitkiesel	Gesammelt von: MESZLÉNYI, B.
3.	Schwach bearbeiteter Quarzporphyrkiesel	Gesammelt von: MESZLÉNYI, B.
4.	Zweikantiger Quarzporphyrkiesel	Gesammelt von: VÁRSZEGI, K.
5.	Zweikantiger Quarzitkiesel	Gesammelt von: JÁMBOR, Á.
6.	Zweikantiger Quarzporphyrkiesel	Gesammelt von: JÁMBOR, Á.
7.	Vierkantiger Quarzporphyrkiesel	Gesammelt von: JÁMBOR, Á.
8.	Dreikantiger Gangquarzitkiesel	Gesammelt von: MESZLÉNYI, B.
9.	Dreikantiger metamorpher Quarzitkiesel	Gesammelt von: JÁMBOR, Á.
10.	Zweikantiger Quarzporphyrkiesel	Gesammelt von: VÁRSZEGI, K.



Aufn.: J. Horváth, T. Füzy

ZUSAMMENFASSUNG

Im westlichen Teil des Mecsek-Gebirges (Süd-Ungarn) befinden sich permische, klastische Gesteine, Sandsteine und Konglomerate an der Oberfläche. Unter Frostwirkung werden die harten Gesteine ziemlich leicht zerkleinert. Während des Pleistozäns wurde auf diesem Weg ein mächtiger (1—20 m) Gehängeschutt auf den Gebirgsfüssen angehäuft. Manche Stücke dieses Gehängeschuttes haben sich — unter dem Einflusse der herrschenden, nordwestlichen Winde — in Dreikanter-Kiesel umgewandelt. Vor der Ablagung des würmischen Lösses haben die Bächer diese Dreikanter umgehäuft; der würmische Löss lagert über diesem Bachschutt. Aus der Karte der Verbreitung der quartären Dreikanter in Ungarn, die ich auf Grund der literarischen Angaben zusammengestellt habe, geht es hervor, dass es nördlich von Nógrád und im südwestlichen Teil Ungarns kein Dreikanter-Vorkommen gibt. Das ist in Zusammenhang damit, dass teils das Ostrowski-Gebirge, teils die Alpen die Kraft der nordwestlichen Winde gebrochen haben, während die Winde auf dem Zwischengebiet den Sand ganz frei herumschleppen konnten.

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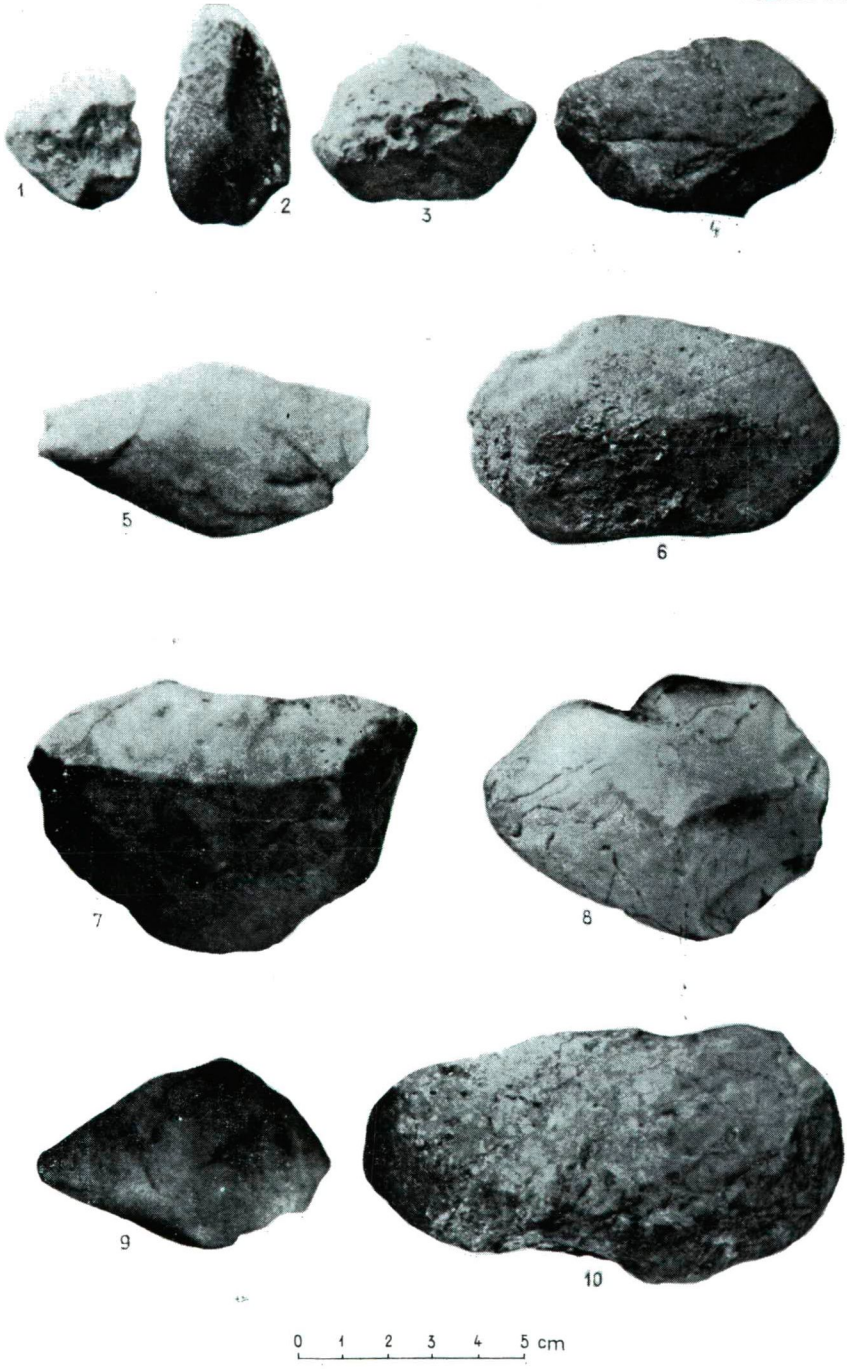
TAFELERKLÄRUNGEN

TAFEL II

Schwächer bearbeitete Fläche der an der Tafel I. dargestellten Dreikanter

1. Fünf schwach entwickelte Flächen sind sichtbar.
2. Auch hier sind drei Flächen entwickelt (mit dünner Kalkschicht).
3. Es sind vier Fläche-„Anlagen" entwickelt.
4. Es sind drei, schwach entwickelte Flächen entstanden.
5. Die ursprüngliche Oberfläche des Kieses ist sichtbar.
6. Zwei, schwach entwickelte Flächen sind mit Kalk inkrustiert.
7. Drei, gut entwickelte Flächen sind zu beobachten.
8. Drei, gut entwickelte Flächen sind zu beobachten.
9. Die ursprüngliche Oberfläche des Kieses ist erhalten.
10. Die ursprüngliche Oberfläche des Kieses ist mit Kalk inkrustiert.

Die Kiese Nos. *1, 2, 3, 5, 7, 8,* und *9* stammen aus der Schicht No. 2 der *Abb. 2,* der Stück No. *4* aus dem südlichsten Lager der *Abb. 3,* der Stück No. *6* aus dem westlichsten und der Kiesel No. *10* aus dem vom südlichsten unmittelbar nach Norden sich befindenden Lager.



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CONTRIBUTION TO THE KNOWLEDGE OF THE MAGNETITE-HEMATITE SYSTEM OF OXYVOLCANITES

by

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INTRODUCTION

In an area of Tertiary volcanism volatile-rich hypomagmatites with crystallization temperatures ranging from 1200°C to 50°C often exhibit various degrees of alteration. These rocks are primarily characterized by volatile-rich minerals of low temperature of formation. One type of these altered rocks is represented by oxyandesites, whose characteristics were described — after SZÁDECZKY-KARDOSS [1958] — by G. PANTÓ [1961]. They are red to red-brown and always connected with an oxidative environment of formation.

In oxyvolcanic masses they are confined to rather narrow zones or bands, though they can be found in the surroundings of volcanic vents too. The unconsolidated porous rock often contains minute hematite platelets of red stain, sometimes visible to the naked eye. The single common feature of these two different types of rock is their colour, as, on the one hand, the hematite occurring in volcanic masses was formed at a high temperature; on the other hand, in the surroundings of volcanic vents hematite may be formed under the influence of volatiles.

It is well-known that whereas in igneous rocks $Fe^{2+} > Fe^{3+}$, in oxyvolcanites an inverse ratio is the case, these rocks being characterized by a higher degree of oxidation. As pointed out earlier [1961, 1964], it would be, however, inadequate to specify a rock merely by its oxidation value. In a study of the possible formation mechanism of oxyvolcanites, SZÁDECZKY-KARDOSS [1953, 1958] concluded that in the case of orthovolcanites at increasing values of the oxidation-reduction potential, first opacitization would take place and thereafter, at higher values, oxyvolcanites would be formed. In the case of metavolcanites the pH value of the solutions also influences rock alteration. As to the oxyvolcanites, there it is after all the magnetite content of the rock that changes into hematite representing a higher degree of oxidation, being responsible, itself, for the highly characteristic red to red-brown stain of the rock.

THE MAGNETITE-MAGHEMITE-HEMATITE SYSTEM

Magnetite and hematite are common accessory minerals of igneous rocks. For this very reason, several workers subjected them to special analysis. Primary hematite only occurs in acid, supersaturated, igneous rocks, being represented chiefly as inclusions in quartz and feldspar as well as in the porous rock of the neighbourhood of volcanic vents. Magnetite, in turn, is common in all types of igneous rocks.

RAMDOHR [1926] found that between Fe_2O_3 and Fe_3O_4 there is an interval of immiscibility, and also that mixing would take place at a high temperature only. At low temperatures the natural magnetite forms, in a great many of cases, a mechanical mixture with hematite, a phenomenon observable under the microscope, but evident from analyses as well.

In the Fe_3O_4–$FeTiO_3$ system the formation temperature of magnetite provides a wide scope for mixing. If in the case of crystalline mixtures of titanomagnetit the melt — the magma — cools quickly, no dissociation will take place. On sloe cooling, however, titanomagnetite will dissociate into magnetite and ilmenite anw the two minerals will be completely interlaced. Relying on the products of naturad dissociation, we may conclude that the beginning of the process is somewherel about the values of 600° and 700°C [1962, 1967].

In the Fe_2O_3-$FeTiO_3$ system of igneous rocks mixing at high temperatures is unlimited. At rapid cooling the mix-crystals are preserved here too, whereas low cooling is associated with dissociation, just as was the case with the former system, but the process is markedly slower compared to titanomagnetite.

GRUNER [1926, 1962] studied magnetites from various localities. He could find no essential difference between the particular types. As believed by him, subaerial magnetite at 150° to 200°C slowly oxidized into hematite and oxidation begins on the (111) faces like in the case of natural martites, above 530°C it changes, however, into another modification. He found the X-ray patterns of martite and hematite identical, but they could always be distinguished from those of magnetite. According to GRUNER, on octahedral faces oxygen can enter the magnetite lattice.

MASON [1943] points out that although numerous varieties of Fe_2O_3 have been described, only two forms of this compound — γ-Fe_2O_3 or maghemite and α-Fe_2O_3 or hematite — are stable in nature, the latter being so at any temperature. Since the alteration of γ-Fe_2O_3 into modification α under natural conditions is a slow process, it occurs even in the nature. The natural formation of maghemite takes place in the zone of oxidation. Although its presence in effusive rocks has also been shown, the influence of thermal water or other agents has always been felt in such cases. Maghemite reacts keenly on metamorphic processes, so its occurrence in older deposits is improbable.

In connection with the relation of martite and maghemite, it should be noted that the original martite is a post-magnetite pseudomorph occurring exclusively in the oxidation zone, being confined to definite crystallographic orientations. On the other hand, maghemitic alteration is controlled by thermal action and independent of crystallographic orientations. Accordingly, martitization and maghemitization are the results of two different genetic processes.

In the typical spinel structure the O^{2-} ions form a face-centered lattice. The cations occupy octahedral and tetrahedral positions between the O^{2-} ions. In the lattice of magnetite one and the same chemical element, iron, occurs in two different positions, thus representing one of the types of the inverse spinel structure. In the

FeO lattice of rock salt-type not all the cationic positions are filled, i. e. the amount of Fe is smaller than would be required by the stoichiometric ratio. The edge of the unit cell of magnetite is of 8,30 Å and includes 32 O^{2-} ions. The number of the Fe^{2+} positions ought to have the same value. Since, however, there is always a shortage of Fe^{2+} and a part of Fe^{2+} changes into Fe^{3+}, the iron ions in the cell occupy but a total of 24 positions, of which 8 are Fe^{2+} ions and 16 are Fe^{3+} ions. If the number of iron ions goes on decreasing to $21\ ^1/_3$ positions, the structure of γ-Fe_2O_3 will result. Thus the increasing substraction — induced lattice failure — will give rise to an increase of the oxidation value.

Earlier DT analyses — known both from literature and our own experience — have unanimously shown [1952, 1957] the existence of well-definable inversion points. Two definite peaks appear — one between 360° and 375°C and one at 580°C. The synthetic magnetites have behaved similarly; the first peak would represent an initial oxidation, the second exothermic one the point of inversion of modification γ- to modification α.

In studying the DTA graph of a natural magnetite from Mineville, LEPP [1957, 1962] also observed two exothermic peaks, but these appeared at 430° and 500°C. The composition of the original substance was close to the ideal one: the Fe_2O_3:Fe_3O_4 ratio was 34 to 66% in a sample heat-treated at 430°C and 45 to 55% at 500°. While analysing X-ray patterns LEPP could observe only the strongest hematite lines beside the lines of magnetite.

Examination of the DTA patterns of magnetites of different genesis permitted to observe that in the case of titanomagnetites (Szarvaskő) the peaks were very indistinct, while for contact-pneumatolitic magnetites (Magyaregregy, Vaskő) very distinct exothermic peaks were obtained at 400°C and 600°C *(Fig. 1)*.

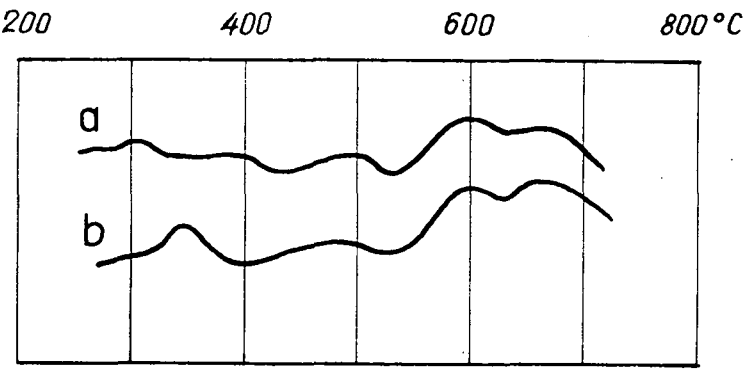

Fig. 1. DTA curves of magnetite samples from *a)* Magyaregregy, *b)* Vaskő (Ocna de Fer)

For the hematites — both the contact-pneumatolitic type (Elba) and the exhalative one (Kakukhegy) — again, distinct peaks were obtained, at 400° and 580°C respectively (for the exhalative type at 400°, 500°, and 600°). Since these minerals always contain some magnetite in form of solid solution, as shown by analyses and observations under the microscope, the aforementioned peaks are likely to represent points of inversion of γ to α *(Fig 2)*. The inversion temperatures

are influenced by the genetic characteristics of the mineral, its impurity, and grain-size.

Consequently, upon changes in temperature the magnetite reacts with changes in structure. As shown by the investigations of HUGGETT and CHAUDRON [1928],

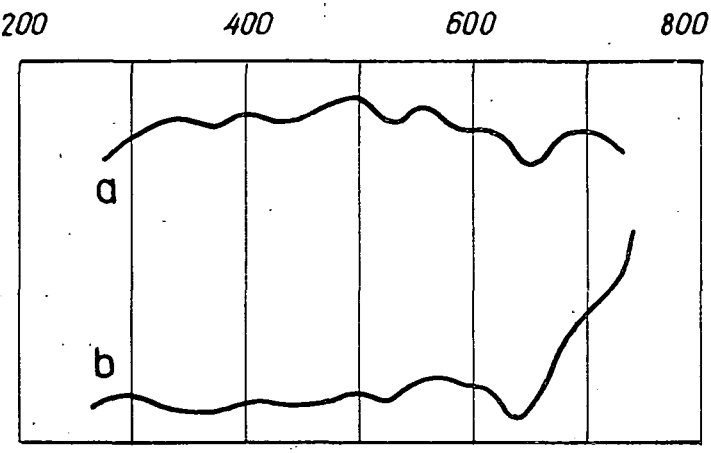

Fig. 2. DTA curves of hematite samples from *a)* Island of Elba, *b)* Kakukhegy (Mt. Cucu)

the susceptibility of magnetite also changes as a function of temperature. In fact a significant change is observed at 570°C — the temperature at which γ-Fe_2O changes into α-Fe_2O_3.

As stated by TWENHOFEL [1927], the „oxidized magnetite" is of magnetic nature' of Fe_2O_3 composition, and it appears, upon oxidation and heating, as an intermediary product between magnetite and hematite. TWENHOFEL believes that the X-ray patterns of both „oxidized magnetite" and magnetite are identical, despite four oxygen atoms have entered the unit cell.

The lattice of hematite is a typical corundum lattice which can be conceived as a rhombohedrally deformed rock salt structure. Accordingly, between magnetite and hematite lattices there is such a marked similarity that the threefold axis of magnetite will become the main axis for hematite.

For the oxidation of magnetite, PAULING and HENDRICKS admitted a volume increase of 5,2%, while the value inferred from density by HISE was as low as 2,5%.

In volcanic tuffs magnetite is often associated with limonite and/or goethite. Since, these too, may undergo oxy-changes, their behaviour upon changes in temperature should also be taken into consideration. Lepidocrocite can only be formed at pH ranging from 2 to 6, thus being uncommon. Limonite and/or goethite undergo gradual changes upon an increase in temperature. After dehydration maghemite and, finally, hematite will result, the process of alteration thus corresponds, after all, to a dehydration or oxidation series, respectively. The effusion of lava on tuffs in volcanic areas is common. The temperature of the lava is higher than the temperature of $\gamma \rightarrow \alpha$-hematite inversion. So the development and occurrence of oxyvolcanite is granted here too.

EXPERIMENTAL RESULTS

For studying the alteration suit of magnetite-maghemite-hematite — or that of magnetite-hematite in the oxyvolcanites — first of all the X-ray diffraction analysis of magnetites and hematites of different genesis was performed. The samples from Magyaregregy (1) and Vaskő (2) represented contact-pneumatolitic magnetite, those of Kiruna the ore-forming magma (3); while the magnetites of Szarvaskő were titanium-bearing (4).

The X-ray diffraction patterns were obtained at Fe Kα radiation with an Mn filter, at 30 kV and 10 mA.

What was analysed was the fraction <0.06 mm of the pure material selected, from the individual samples.

The values obtained for the pure substances are given in Table I.

Accordingly, in the above samples the characteristic values of d_{hkl}, *311*, *511*, *220* and *440*, did exist. The lattice planes (*111*) parallel to the octahedral face

Table I

1			2			3			4		
d	*hkl*	*I*	*d*	*hkl*	*I*	*d*	*hkl*	*I*	*d*	*hkl*	*I*
										olivin	
									5.142	021	1.5
4.803	111	1	4.834	111	1	4.845	111	2.5	4.848	111	1
						4.286	200	5			
									3.912	olivin	1.5
									3.740	ilm.	
										102	3
3.246		1				3.269		2	3.273	amf.?	1.5
						3.124		2	3.133	amf.?	10
2.973	220	3	2.965	220	6	2.973	220	8			
2.784	300;	2				2.796	300;	6.5	2.796	300;	7
	221						221			221	
									2.745	ilm.	2
										104	
2.521	311	10	2.526	311	10	2.532	311	10	2.532	311	10
									2.476	ol.	4
2.413	222	1	2.408	222	1	2.422	222	1			
2.303	320?	1				2.319	320	3	2.292	320?	7
			2.197	321	2						
			2.094	400	4	2.094	400	6			
						1.886	420	1	1.900	420	1
									1.821	ilm.	1
										204	
1.777	322?	1				1.780	322?	2			
									1.758	amf.?	1
1.711	422	2	1.711	422	2	1.711	422	3.5	1.722	422	3
										ilm. 116	
1.631	431:	2				1.634	431:	2	1.650		2
	510						510				
1.609	333;	5	1.611	333;	5	1.614	333;	8			
	511			511			511				
									1.498	ilm.	10
										214	
									1.493	440?	5
1.484	440	7	1.483	440	4	1.484	440	8,5			

were, as a rule, poorly represented. In the titanomagnetite of Szarvaskő, along with the strongest line, 2.53, representing magnetite, the ilmenite was also represented by a distinct line ($d = 1.498$).

The X-ray diffraction values obtained for these same samples, after temperation at 400°C for 20 hours, were as follows (Table II).

Table II

1			2			3			4		
d	*hkl*	*I*	*d*	*hkl*	*I*	*d*	*hkl*	*I*	*d*	*hkl*	*I*
			4.834	111	2	2.834	111	1½	4.724	111	2
									4.599		1
			3.905		1	3.827		1/2	3.946		4
3.680?		1	3.676		1				3.765	ilm.	2
						3.555		1/2	3.533		1
			3.255		1	3.201		1/2	3.261		1
3.031		2							3.003		2
2.958	220	4	2.973	220	5	2.970	220	3	2.958	220	1
									2.885		10
			2.784	300	1	2.787	300	1/2	2.800	ilm.	10
										204	
									2.751	amf.?	8
2.695		3	2.701		3	2.695		2			
2.519	311	10	2.529	311	10	2.524	311	10	2.534	311	2
									2.480		2
			2.430		1	2.422		1			
			2.315		1	2.307		1/2	2.282		8
									2.168		1
2.091	400	2	2.099	400	2	2.096	400	3			
									2.015		1
1.924		1							1.924		1
1.916		1							1.901	420	6
									1.866		3
			1.840	420	2				1.840	204	2
									1.788	amf.	4
									1.723	ilm.	2
										116	
1.693		1	1.694	422	1	1.692	422	1/2			
1.612	333;	2				1.615	511;	4	1.632	431;	1
	115						333			510	
1.484	440	4	1.595		5	1.483	440	3			
			1.485	440	5						
1.455		1	1.455		1	1.452		1/2	1.467	440	1
1.445		1	1.423		1	1.448		1/2	1.442		1

Upon heating, the samples showed no change in colour. No substantial changes in the characteristic d_{hkl} values could be observed. The only sample in which (*111*) $d = 4.83$ failed to occur was that of Magyaregregy, while in the rest of the samples even the intensity has remained unchanged. The characteristic $d = 2.52$ (*311*) has been preserved with invariable intensity. In the samples from Vaskő, Magyaregregy, and Kiruna a mean intensity of $d = 1.48$ was also characteristic. These characteristics were somewhat less marked (*400*). Though of lower intensity, (*220*) ($d = 2.97$) has also been preserved. As for $d = 1.61$ (*511*; *333*), it lacks completely in the Vaskő sample, being represented with a lower intensity in the rest of the samples as well.

In the case of the titanomagnetite of Szarvaskő the heated samples locally showed a rather marked presence of ilmenite; at the same time, the lattice plane

characterized by d = 1.478 and by an index of *214* disappeared in the heated sample, although it had been represented with an intensity amounting to 10 in the original sample.

Thus, we may conclude that upon a long-lasting heat-treatment at 400°C no substantial structural change takes place.

Of the maghemite values quoted in literature, the lattice planes parallel to hexahedral, rhombdodekahedral, and deltoidikositetrahedral faces are characteristic. These did exist here: $d_{hkl} = 440, 400, 311, 511$. As for γ-Fe_2O_3, it has a lattice similar to that of magnetite, except for its deficiency of iron.

During the 10-hour heat-treatment of these samples at 600°C the following striking changes in colour were observed; dark-red, brownish-red. The changes in the value of oxidation thus could be observed. The scratch of samples like these was also found to be red, a phenomenon typical of hematite. The X-ray diffraction values of the samples are given in Table III.

Table III

1			2			3			4		
d	*hkl*	*I*	*d*	*hkl*	*I*	*d*	*hkl*	*I*	*d*	*hkl*	*I*
									10.008		2
									9.417		2
						5.361		2.5			
			4.803		1.5	4.823		1	4.855		1
						4.215		1			
									4.066		1.5
3.687	$01\bar{1}2$	1							3.692	$\bar{1}2\bar{1}3$	6
						3.555		1			
									3.339		1.5
3.270		1									
						3.228		5			
									3.113	1	
						3.079		4			
2.973	211	4	2.960	211	3.5				2.977	211	5
2.790		4	2.773		1	2.773	ilm.	1	2.787		1.5
2.705	$10\bar{1}4$	5	2.677	$10\bar{1}4$	2	2.677	$10\bar{1}4$	1	2.707	$10\bar{1}4$	10
									2.540	ilm.	7
2.528	$11\bar{2}0$	10	2.513	$11\bar{2}0$	10	2.519	$11\bar{2}0$	4	2.521	$11\bar{2}0$	7
									2.485		1
2.312		1									
						2.214	$11\bar{2}3$	1	2.208	$11\bar{2}3$	3
						2.137		4			
2.092		4	2.086		6				2.101		1
									2.032		1.5
						1.931		1			
1.842		1							1.840		4
						1.814		1			
						1.794		1	1.793		1
						1.753		5	1.764		1.5
									1.714		1
1.696	$11\bar{2}6$	1.5	1.708	$11\bar{2}6$	1.5	1.681	$11\bar{2}6$	2	1.695	$11\bar{2}6$	5
1.634	$21\bar{3}1$	1				1.648	$21\bar{3}1$	10	1.637	$21\bar{3}1$	1.5
1.609	$01\bar{1}8$	2	1.609	$01\bar{1}8$	4	1.620		1	1.613	$01\bar{1}8$	1
	$12\bar{3}2$			$12\bar{3}2$						$12\bar{3}2$	
1.481	$21\bar{3}4$	4	1.483	$21\bar{3}4$	4				1.489	$21\bar{3}4$	4
1.448	$30\bar{3}0$	2		$30\bar{3}0$					1.453	$30\bar{3}0$	2

Considering the values quoted in literature with reference to hematite, these readily correspond to the values obtained here. The characteristic lattice planes indexed *10$\bar{1}$4*, *11$\bar{2}$0*, *21$\bar{3}$4*, and *30$\bar{3}$0* are encountered here too. For the Szarvaskő sample, the characteristics of ilmenite can be found associated with those of hematite. In this sample we have to reckon with residues of magnetite — as shown even by the ore microscope — which may be accounted for by the fact that MgO hinders $\gamma \rightarrow \alpha$ alteration. By the way, the presence of magnetite in these rocks should be allowed for even on the basis of the olivine content of the country rock. This is warranted by analyses. Although ilmenite and hematite are similar structures and though Fe and Ti ions of regular distribution occur in ilmenite, the patterns of the two minerals can be readily distinguished from one another.

The X-ray analyses of the magnetite — γ-Fe_2O_3 — α-Fe_2O_3 series led BASTA [1959] to the conclusion that the calculated lattice constant gradually decreased with increasing temperature, to turn again into an increases above the inversion point of modification α. This fact proved true for the investigations under consideration.

As shown by the results of investigations, modification α-Fe_2O_3 is usually stable above 600°C. For this reason, X-ray patterns as bases of comparison were also obtained for a few samples of pure hematite. So the contact-pneumatolitic type has been confronted with a sample of Elba (1), the exhalative type with one from Kakukhegy (2), and the sedimentary type with the red ochre of Podagrec (3). These data are given in Table IV.

Table IV

1				2				3			
d	*hkl*	*hkīl*	*I*	*d*	*hkl*	*hkīl*	*I*	*d*	*hkl*	*hkīl*	*I*
				4.302			1				
4.028	110	01$\bar{1}$2	1	4.007	110	01$\bar{1}$2	2.5				
3.652	101	1$\bar{1}$02	6	3.640	101	1$\bar{1}$02	8	3.699	101	1$\bar{1}$02	2
2.955	112	01$\bar{1}$4	3	2.948	112	01$\bar{1}$4	2				
2.757	101	11$\bar{2}$0	1.5	2.751	101	11$\bar{2}$0	1				
2.682	211	10$\bar{1}$4	10	2.674	211	10$\bar{1}$4	10	2.699	211	10$\bar{1}$4	9
2.503	101	11$\bar{2}$0	8.5	2.503	101	11$\bar{2}$0	7.5	2.508	101	11$\bar{2}$0	10
2.422	102	$\bar{1}$2$\bar{1}$3	1	2.417	102	$\bar{1}$2$\bar{1}$3	1				
2.192	210	11$\bar{2}$3	2	2.191	210	11$\bar{2}$3	2.5	2.204	210	11$\bar{2}$3	2
				2.065	200	20$\bar{2}$2	1				
2.015	202	2$\bar{2}$04	1.5	2.015	202	2$\bar{2}$04	1				
1.859	123	11$\bar{2}$0	1	1.857	123	11$\bar{2}$6	1	1.845	123	11$\bar{2}$6	2
1.832	220	02$\bar{2}$4	8.5	1.832	220	02$\bar{2}$4	4				
1.726			5								
1.687	321	11$\bar{2}$6	1	1.687	321	11$\bar{2}$6	4	1.692	321	11$\bar{2}$6	4
1.631	201	21$\bar{3}$1	1.5	1.634	201	21$\bar{3}$1	1	1.644	210	21$\bar{3}$1	5
				1.628			1				
1.593	233	10$\bar{1}$8	2	1.594	233	10$\bar{1}$8	3	1.598	233	10$\bar{1}$8	1
		01$\bar{1}$4				01$\bar{1}$4				01$\bar{1}$4	
1.566			1								
1.539			5					1.525			1
								1.500			1
1.479	310	21$\bar{3}$4	6	1.483	310	21$\bar{3}$4	3	1.483	310	21$\bar{3}$4	1
								1.475			1
1.451	331	02$\bar{2}$7	1	1.451	331	02$\bar{2}$7	8	1.452			1
	211	30$\bar{3}$0			211	30$\bar{3}$0					

The data correspond well to those magnetite held at 600°, consequently, the change of magnetite into hematite takes place after a comparatively short heat treatment. This means that even the heat of a volcanic lava may provoke the formation of oxyvolcanites. In the hematites of volcanic origin the prevalence of completely flat rhombohedral lattice planes is quite distinct, as opposed to the case of the Elba and Podagrec types where these are manifested by poor intensities.

Upon heating, changes in the degree of oxidation take place in other iron compounds liable to breakdown too. From this point of view the study of siderite was carried out.

The thermal dissociation of siderite takes place between 500° and 600°, in dependence on the size of the crystal grains, on the one hand, and on the presence of Mn^{2+} and Mg^{2+} ions, on the other. After the siderite has broken down into FeO and CO_2, an exothermal process will lead to the oxidation of FeO to Fe_2O_3. In Table V the X-ray diffraction values obtained for a fresh siderite sample from Rudnany (1) and for the same siderite after a 10-hour treatment at 700° (2) are given.

Table V

1			2		
d	*hkīl*	*I*	*d*	*hkīl*	*I*
4.155		1			
3.905		1			
			3.676	$01\bar{1}2$	3
3.589	$10\bar{1}2$	3			
3.078		3			
			2.965		2
2.787	$10\bar{1}4$	10			
			2.692	$10\bar{1}4$	10
			2.519	$11\bar{2}0$	6
2.339	$11\bar{2}0$	2			
			2.202	$11\bar{2}3$	2
			2.189		1.5
2.154	$11\bar{2}3$	1/2			
2.123		1			
			2.096	$20\bar{2}2$	1
1.950	$20\bar{2}2$	6			
1.903		1/2			
1.891		1/2			
			1.838	$02\bar{2}4$	3
1.758		2			
1.718	$11\bar{2}6$	3			
			1.694	$11\bar{2}6$	3
			1.616	$21\bar{3}1$	1
			1.597	$12\bar{3}2$; $01\bar{1}8$	1
			1.485	$21\bar{3}4$	3
			1.453	$02\bar{2}7$; $30\bar{3}0$	2

As evident from the tabulation, after heating siderite lost all its original characteristics; on the other hand, the characteristic *d* values of hematite, 2.69, 3.67, 2.51, 1.48, 1.45, did appear, while none of the lines of siderite was preserved, despite the presence of identical crystal classes.

Since in volcanic rocks too it is the magnetite of lava rocks, and the magnetite or limonite and goethite of volcanic tuffs that is altered under oxidative conditions

on the surface or close to it, magnetite separated from ground pyroxenic andesite samples of 0.06 mm grain size by using a magnet tool was also studied. The X-ray patterns obtained for these samples and for those heated to 600°C permitted to evaluate the process of magnetite-hematite alteration. In oxy-tuffs similarly the presence of hematite could be shown.

CONCLUSIONS

It can be stated that the red stain of volcanic rocks is always due to the presence of hematite. In the surroundings of volcanic vents or along cracks, where the escape of iron chloride and vapour can be allowed for, hematite may form even primarily. Such a rock is usually porous, and of red stain. Another mechanism of the red stain of volcanic rocks consists in that a lava of high temperature flows over an earlier volcanic rock and a red, so-called oxyvolcanite band varying in thickness in dependence on the volume of the lava is formed at the contact of the two rocks. If the lava flows over volcanic tuffs, the escaping vapour will produce a vesicular, scoriaceous rock — similarly red because of secondary hematite — on the boundary of the two rocks. Since the pressure is comparatively higher here because of the vapour formed in the rock, this condition is favourable for the development of modification α which is already stable in contrast with γ-Fe_2O_3. The transformation of $\gamma \rightarrow \alpha$ represents, at the same time, a *monotropic polymorphy*, as α-Fe_2O_3 does not regenerate to modification γ. This type of alteration also takes place under natural conditions on the surface, but this is extremely slow process, so that modifications γ and α may occur together.

Since primary hematite as an accessory mineral can only occur in igneous rocks abundant in silica, the total hematite content of oxyvolcanites and volcanic tuffs should be regarded as secondary.

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LITHOLOGICAL AND GEOLOGICAL STUDY OF THE PLIOCENE FORMATIONS IN THE DANUBE—TISZA INTERSTREAM REGION

Part II.

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In the first part of the paper the deposition, grain size distribution, heavy mineral composition, sources and directions of denudation of the Pliocene formations of the Danube—Tisza Interstream Region were dealt with. The following discussion will be devoted to such chemical characteristics of these sediments as may also contribute to the better understanding of their history of evolution.

CALCIUM CARBONATE CONTENT

It was calculated from the weight of loss of CO_2 as found after attacking 5-gram-samples by hydrochloric acid.

The carbonate content of the *Lower Pannonian* sediments (Table II samples Nos 120—129) from the northern part of the investigated area of the region *(Fig. 1)* averages about 25%. Merely two samples (Nos 122 and 128) do show striking values (64 and 68%, respectively).

In the SW part of the region (Érsekcsanád, Rém, and Jánoshalma) the average carbonate content of the Lower Pannonian sediments (Table II, samples Nos 130—139) is higher, attaining 50%. These samples were taken in a zone, where, as shown elsewhere, the basement has remained in a higher structural position [G. CSIKY 1966, B. MOLNÁR 1966*e*]. L. KÖRÖSSY [1962] believes that in those parts of the Hungarian Basin where Mesozoic limestones occur near-by, the carbonate content of the Pannonian sediments is higher than elsewhere. The highly calcareous ranges of Mts. Mecsek and Mts. Villány extend to the W from the area under consideration. Thus, the higher carbonate content of the Lower Pannonian in the adjacent SW part of the Danube—Tisza Interstream Region may derive from these sources *(Fig. 1)*. Accordingly the heavy mineral analyses have also suggested a denudation direction from W toward E [B. MOLNÁR, 1966*a*, *e*, *f*].

The Lower Pannonian sediments overlying the deeper-sunken part of the basement (Tables I and II, samples Nos 140—169) contain less calcium carbonate, averaging

from 15 to 30%. Similar results were obtained by M. MUCSI [1967] and I. RÉVÉSZ [1967] for the corresponding layers cut by a borehole near Szeged (Algyő) and by one at Ásotthalma, respectively (1967).

The distance of this area from Mts. Mecsek and Mts. Villány may account for the lower carbonate content. The relatively coarser grain size and its quick

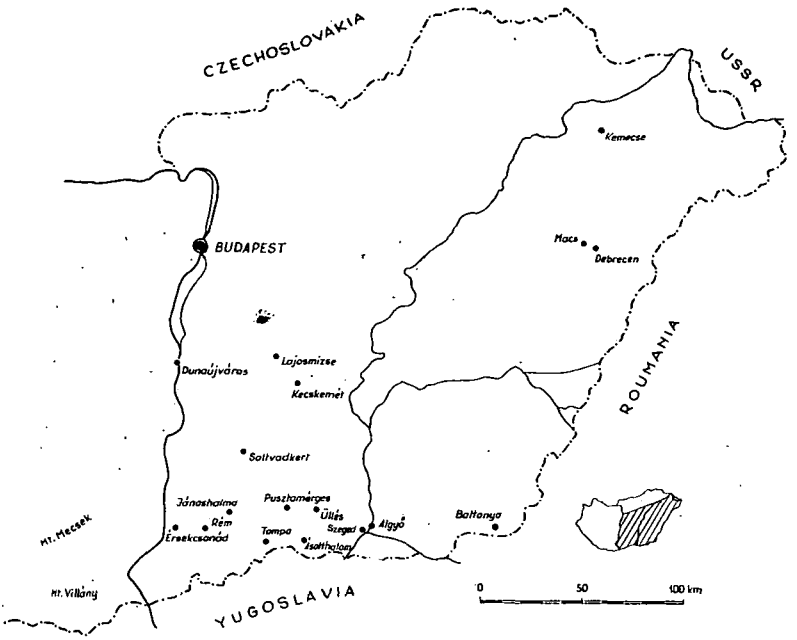

Fig. 1. Layout of the boreholes studied

alternating development, respectively, compared to that of observed in the western part, testifies to shallower depth of sedimentation. This could hardly favour a greater accumulation of carbonates under the less undisturbed conditions of sedimentation.

The carbonate content of the *Upper Pannonian* formation varies between 0 and 39%, attaining, on the average, from 20 to 30% (Tables II—VI, samples N^{os} 20—119.). There is no striking value that found for the Lower Pannonian. In the Mts. Mecsek and Mts. Villány as well as in their vicinity the Upper Pannonian formation is discordantly settled over the Lower Pannonian even surpassing it [GY. WEIN, 1962]. Consequently, the area emerging from the inland sea, accessible for erosion, was reduced, so such an amount of calcium carbonate as in the case of Lower Pannonian could not be dissolved. In addition, the Upper Pannonian sedimentation of the Hungarian Basin took more and more of variable character and the environment did no longer favour the accumulation of carbonate.

Hence, in the Upper Pannonian the various parts of the area studied cannot be plainly distinguished on the basis of the carbonate content. It is alone the surroundings of Szeged that seem to be conspicuous for a somewhat lower carbonate content, compared to the rest of the area. Of course, this figure, 10—20%, can be ascribed to the same causes as was the case with the Lower Pannonian.

Thus, the carbonate content of the Lower Pannonian formation of the region

Table I

Number	Boring		Type of sediment	$CaCO_3$ %	Total salt %	pH (H_2O)	Age	
	Locality	Depth m						
146.	Üllés—1	1480—1486/a	Small sand, medium sand and fine silt alternately settled light gray and yellowish-brown	33,2	0,08	8,7		
147.	Üllés—1	1480—1486/b	Mudstone, yellowish-brown	19,9	0,09	8,6		
148.	Üllés—1	1586—1589,5	Mudstone, yellowish-brown	24,4	0,09	8,8		
149.	Üllés—1	1652,5—1655	Mudstone with embedded small sand, light gray	15,4	0,03	9,2		
151.	Üllés—1	1782—1783,5	Mudstone, dark gray	17,7	0,10	8,7		
152.	Üllés—1	1828—1830	Mudstone, dark gray	11,1	1,06	8,9		
153.	Üllés—1	1885—1890	Claystone, brownish gray	11,1	0,03	9,0		
154.	Üllés—2	1479—1481,5	Mudstone, gray	22,1	0,07	8,8	PLIOCENE	LOWER PANNONIAN
155.	Üllés—2	1638—1644	Small-grained sandstone, light gray	19,0	0,00	8,8		
156.	Üllés—2	1703—1705	Claystone and finegrained sandstone alternately brownish-gray	13,3	0,07	8,8		
157.	Üllés—2	2188,5—2189,5	Mudstone, dark-gray	28,8	0,03	9,1		
158.	Üllés—7	1556,5—1562	Mudstone and fine-grained sandstone alternately, brownishgray	18,5	0,00	9,4		
159.	Üllés—7	1598—1604	Mudstone, light gray	24,4	0,00	9,3		
160.	Üllés—7	1646—1652	Mudstone, with plant rests, gray	19,9	0,00	9,4		
161.	Üllés—7	1705—1706	Mudstone, with plant rests, gray	19,9	0,03	9,2		
162.	Üllés—7	1799—1805	Mudstone with plant rests, darkspotfed gray	13,3	0,03	9,3		
163.	Üllés—8	1624—1627	Mudstone, yellowish-brown	19,9	0,03	9,0		
164.	Üllés—8	1660—1664	Silt with embedded diagenized sandstone, light gray	36,8	0,00	8,8		
165.	Üllés—8	1765—1770	Silt with embedded diagenized sandstone, light gray	24,4	0,03	9,0		
166.	Üllés—8	1842,5—1843	Claystone, greenish-gray	15,5	0,06	8,9		
167.	Üllés—8	2044—2048	Claydtone with plant rests, dark gray	25,7	0,05	9,2		
168.	Üllés—8	2139—2141	Fine-grained sandstone, strongly micaceous, gray	26,6	0,00	9,2		
169.	Üllés—8	2145—2149	Small-grained sandstone with embedded silt, light gray	26,6	0,00	8,8		

Table II

Number	Boring: Locality	Boring: Depth	Type of sediment	$CaCO_3$ %	Total salt %	pH (H_2O)	Age	
116.	Szeged, Székelysor	1595—1596,2	Mudstone, yellowish-gray	4,4	0,04	9,2		UPP. PANN.
117.	Szeged, Székelysor	1697—1698	Small sand, with medium-grained part, calcareous, light gray	11,1	0,00	8,8		
118.	Szeged, Székelysor	1785—1787,4	Friable small-grained sandstone	6,6	0,00	9,0		
119.	Szeged, Székelysor	1893—1894,5	Claystone, dark greenish-gray	8,9	0,08	9,2		
120.	Dunaújváros—1	777,5—779,5/a	Mudstone with plant rests	19,9	0,14	9,0	PLIOCENE	LOWER PANNONIAN
121.	Dunaújváros—1	777,5—779,5/b	Claystone, dark gray	6,6	0,14	9,0		
122.	Lajosmizse—3	945—947	Limy marl, gray	64,2	0,20	9,1		
123.	Kecskemét Ny—1	1169—1174	Clayey fine silt, lightly diagenized, greyish-brown	22,1	0,10	8,8		
124.	Kecskemét Ny—1	1182—1186/a	Small sandy fine sand, light gray	33,2	0,00	9,2		
125.	Kecskemét Ny—1	1182—1186/b	Medium sand. with small sand. gray	31,0	0,00	9,3		
126.	Kecskemét Ny—1	1567—1571	Claystone with plant rests, gray	28,8	0,12	9,0		
127.	Kecskemét Ny—1	1594—1595	Claystone shell-like fractured, with mollusc and plant rests, brownish-gray	35,0	0,12	8,9		
128.	Soltvadkert—1	1073—1077	Limy marl, gray	68,6	0,10	9,2		
129.	Soltvadkert—1	1116—1122	Clay, light gray	26,6	0,09	9,4		
130.	Érsekcsanád—1	354—358,4	Mudstone, shell-like fractured, with plant rests, light-gray	52,0	0,08	9,3		
131.	Rém—2	550—554	Fine silty clay, shell-like fractured, with plant rests, light-gray	48,7	0,11	7,8		
132.	Rém—2	574—577	Limy marl, gray	75,3	0,20	7,7		
133.	Rém—2	610—614,5	Limy marl, light gray	66,4	0,15	7,9		
134.	Rém—2	665—669	Clayey marl, light gray	66,4	0,14	7,7		
135.	Jánoshalma—7	450—455	Clay shell-like fractured, light	28,8	0,22	8,1		
136.	Jánoshalma—7	499,5—504	Clayey marl	64,2	0,16	8,2		
137.	Jánoshalma—7	550—555	Fine silt, shell-like fractured, light gray	11,1	0,16	8,4		
138.	Jánoshalma—7	679—684	Clayey marl light gray	51,8	0,10	8,9		
139.	Tompa—7	449,5—455	Coarse silty fine silt	11,1	0,06	9,2		
140.	Pusztamérges—2	526—531	Fine silty coarse silt, badly assorted, brownish-yellow	33,2	0,05	9,1		
141.	Pusztamérges—2	576—581	Lightly diagenized fine silty clay, gray	22,1	0,16	8,4		
142.	Pusztamérges—2	600—605	Lightly diagenized fine silty clay, gray	22,1	0,16	8,7		
143.	Pusztamérges—2	625—629,5/a	Fine silty clay, shell-like fractured	19,9	0,10	8,9		
144.	Pusztamérges—2	625—629,5/b	Clayey fine silt, yellowish gray	35,4	0,12	8,8		
145.	Üllés—1	1371—1376	Claystone, lightly diagenized, light brownish-gray	22,1	0,07	9,1		

Table III

Number	Boring		Type of sediment	$CaCO_3$ %	Total salt %	pH (H_2O)	Age	
	Locality	Depth m						
87.	Üllés—2	776—782/a	Coarse silty fine silt, light gray	15,5	0,00	9,6		
88.	Üllés—2	776—782/b	Fine silty clay, light gray	33,2	0,09	9,1		
89.	Üllés—2	870—871,3	Coarse silt, light gray	33,2	0,03	9,2		
90.	Üllés—2	1129—1135	Small sand, with mollusc rests, ligth gray	24,4	0,07	9,0		
91.	Üllés—2	1194—1200	Fine sandy small sand light gray	19,9	0,09	8,5		
92.	Üllés—2	1361,5—1367,5	Mudstone with interbedded fine-grained sandstone, gray	22,1	0,06	9,0		
93.	Üllés—2	1405—1408	Mudstone, light gray	16,5	0,07	8,9		
94.	Üllés—7	1016—1022	Fine silt and small sand alternately, light gray	19,9	0,02	8,6		
95.	Üllés—7	1150—1156/a	Fine silt, with plant rests, brownish-gray	19,9	0,02	8,5		
96.	Üllés—7	1150—1156/b	Fine silt with lignite stripes	0,00	0,06	9,2		
97.	Üllés—7	1186—1192	Clayey fine silt, light gray	24,4	0,06	9,2		
98.	Üllés—7	1232—1237	Small sand with few medium grainned part, light gray	15,5	0,00	9,3		
99.	Üllés—7	1317—1323	Friable small-grained sandstone light gray	15,5	0,00	9,2		
100.	Üllés—8	1155—1161	Mudstone, yellowish-gray	19,9	0,04	9,1		
101.	Üllés—8	1255—1258	Mudstone, yellowish-gray	26,6	0,04	9,1		
102.	Üllés—8	1362—1367	Small sand, light gray	9,7	0,00	9,1		
103.	Szeged, Textil. M.	996—997,5/a	Claystone, greenish gray	33,2	0,10	8,8		
104.	Szeged, Textil. M.	996—997,5/b	Strongly clayey fine silt, gray	13,2	0,07	8,2		
105.	Szeged, Textil. M.	997—1000/a	Coarse silty fine silt with mollusc rests, gray	11,1	0,07	8,7		
106.	Szeged, Textil. M.	997—1000/b	Fine silty coarse silt, gray	8,9	0,06	8,6		
107.	Szeged, Textil. M.	1500	Fine silty coarse silt, gray	0,00	0,00	8,0		
108.	Szeged, Textil. M.	1600	Medium sand, light gray	8,9	0,00	8,0		
109.	Szeged, Székelysor	829,5—831	Silt, dark gray	8,9	0,06	9,2		
110.	Szeged, Székelysor	990—992	Small sand with medium-grained part, light gray	2,2	0,00	8,7		
111.	Szeged, Székelysor	1098—1100	Fine sand, light gray	11,1	0,00	9,1		
112.	Szeged, Székelysor	1193—1194	Fine silty clay, greenish-gray	2,2	0,10	8,7		
113.	Szeged, Székelysor	1294—1295,5	Clay, with interbedded small sand, greenish gray	17,7	0,19	8,3		
114.	Szeged, Székelysor	1490—1491,5/a	Fine silt, with interbedded coarse silty fine sand, gray	31,0	0,00	8,7		
115.	Szeged, Székelysor	1490—1491,5/b	Spotted clay, dark gray, strongly humous	0,00	0,50	4,5		

Table IV

Number	Boring		Type of sediment	$CaCO_3$ %	Total salt %	pH (H_2O)	Age	
	Locality	Depth m						
60.	Jánoshalma—7	300—304	Fine sand, light gray	19,9	0,00	8,2		
61.	Jánoshalma—7	356—357,5	Clayey fine silty coarse silt, light gray, shell-like fractured	22,1	0,10	8,6		
62.	Tompa—7	225—230,5	Fine silt, light gray	31,0	0,00	8,4		
63.	Tompa—7	275—280	Coarse silty fine silt	17,7	0,06	9,1		
64.	Tompa—7	302—307,5	Clayey coarse silty fine silt, ochre-spotted light gray	26,6	0,05	9,2		
65.	Pusztamérges—2	200—205,5/a	Coarse silty fine silt, yellowbrownish gray	22,1	0,10	7,7		
66.	Pusztamérges—2	200—205,5/b	Fine silty clay, gray, calcareous spotted	22,1	0,07	7,9		
67.	Pusztamérges—2	250—255,5	Fine silty, caly brownish-gray	4,4	0,03	9,4		
68.	Pusztamérges—2	351—356	Strongly coarse silty fine silt, spotted with plant rests	11,1	0,09	9,3	PLIOCENE	UPPER PANNONIAN
69.	Pusztamérges—2	431—436	Coarse silty fine silt light yellowish-gray	6,6	0,08	9,0		
70.	Pusztamérges—5	350—355	Clay, dark gray (spotted)	13,2	0,10	9,2		
71.	Pusztamérges—5	450—455/b	Fine silty coarse silt, light gray	6,6	0,08	8,5		
72.	Üllés—1	760—766/a	Clayey fine silt, light gray, strongly (calcareous spotted) humous.	27,5	0,18	7,6		
73.	Üllés—1	760—766/b	Coarse silt, light gray	16,4	0,07	9,0		
74.	Üllés—1	833—839/a	Fine silt with interbedded fine sand, light gray	16,4	0,05	8,9		
75.	Üllés—1	833—839/b	Fine silty clay light brownish-gray.	18,6	0,16	8,2		
76.	Üllés—1	915—919/a	Fine silt, light yellow	38,5	0,10	8,3		
77.	Üllés—1	915—919/b	Coarse silty fine silt, light yellowish-gray	25,2	0,07	8,4		
78.	Üllés—1	946—968/a	Fine silty clay with carbonaceous stripes, dark gray	7,5	0,07	8,7		
79.	Üllés—1	946—968/b	Fine silty clay, light greyishyellow	29,7	0,07	8,7		
80.	Üllés—1	1000—1006/a	Clayey silt, lightly diagenized light yellowish-gray	18,7	0,09	8,5		
81.	Üllés—1	1000—1006/b	Clay, carbonaceous mollusc and shell rests, dark gray	0,00	0,16	7,9		
82.	Üllés—1	1064—1070/a	Mudstone, light gray	38,5	0,05	9,1		
83.	Üllés—1	1064—1070/b	Mudstone, light gray	18,7	0,14	8,8		
84.	Üllés—1	1144—1150	Claystone greyish yellowishbrown	15,4	0,12	8,4		
85.	Üllés—1	1217—1223	Fine silty coarse silt light yellowish-gray	23,0	0,07	8,5		
86.	Üllés—1	1310—1315	Small- and fine-grained sandstone, light brown	36,3	0,05	9,1		

Table V

Number	Boring: Locality	Boring: Depth m	Type of sediment	$CaCO_3$ %	Total salt %	pH (H_2O)	Age	
31.	Dunaújváros—1	551—553/b	Coarse silty fine silt, dark gray, with plant rest	35,4	0,08	8,2		
32.	Dunaújváros—1	553—557	Coarse silty fine silt, yellow, with plant rests	33,2	0,00	8,3		
33.	Dunaújváros—1	603—605	Coarse silty fine silt, dark gray	26,6	0,08	8,9		
34.	Dunaújváros—1	651—653	Fine silty coarse silt, light gray	27,5	0,00	9,0		
35.	Dunaújváros—1	699,5—701,5	Fine silty coarse silt, dark gray	24,4	0,07	9,1		
36.	Lajosmizse—3	505—510/a	Coarse silty fine silt, light gray	24,4	0,10	9,1		
37.	Lajosmizse—3	505—510/b	Fine silty clay, light gray	26,6	0,10	9,1		
38.	Lajosmizse—3	600—606	Coarse silty fine silt, light gray	31,0	0,16	9,5		
39.	Lajosmizse—3	700—705	Clayey, coarse silty fine silt, light gray	28,8	0,11	9,2		
40.	Lajosmizse—3	750,5—755,5	Clayey, coarse silty fine silt, light gray	35,4	0,18	9,6		
41.	Lajosmizse—3	805—806	Clayey fine silt, shell-like fractured, light gray	22,1	0,16	9,4		
42.	Lajosmizse—3	890—892	Clayey fine silt, shell-like fractures, lightly diagenized, gray	19,9	0,18	9,0		
43.	Kecskemét Ny—1	646—651,5/a	Coarse silt and fine silt alternately, light gray	33,2	0,08	9,1		
44.	Kecskemét Ny—1	646—651,5/b	Coarse silty fine sand, light gray	24,4	0,06	8,5		
45.	Kecskemét Ny—1	760—765/a	Small sand. partly medium-grained. light gray	19,9	0,00	9,0		
46.	Kecskemét Ny—1	760—765/b	Clayey fine silt, shell-like fractured, light gray	24,4	0,10	8,9		
47.	Kecskemét Ny—1	760—765/c	Fine silty coarse silt, greyish brown	28,8	0,09	8,8		
48.	Kecskemét Ny—1	901—907/a	Fine sandy small sand, light gray	28,8	0,07	8,5		
49.	Kecskemét Ny—1	901—907/b	Small sand, with carbonaeous stripes, considerably micaceous, light gray	26,6	0,12	8,2		
50.	Soltvadkert—1	557—562	Clayey coarse silty fine silt, light gray	29,8	0,00	8,9	PLIOCENE	UPPER PANNONIAN
51.	Soltvadkert—1	646—651/a	Clayey fine silt, shell-like fractured, light gray	24,4	0,07	8,7		
52.	Soltvadkert—1	646—651/b	Coarse silty fine silt, light gray	24,4	0,07	8,7		
53.	Soltvadkert—1	912—917	Fine silty clay, gray	28,8	0,09	9,0		
54.	Érsekcsanád—1	252—257	Coarse silty fine silt, shell-like fractured, light gray	26,6	0,09	7,8		
55.	Érsekcsanád—1	295—300	Clayey fine silt, shell-like fractured, lightly diagenized	22,1	0,09	7,9		
56.	Érsekcsanád—1	324,5—329,5	Fine silty clay, shell-like fractured, lightly diagenized	26,6	0,14	7,6		
57.	Rém—2	201—206	Clayey coarse silty fine silt spotted gray	6,6	0,00	8,3		
58.	Rém—2	450—455	Fine silty clay, shell-like fractured	26,6	0,20	7,8		
59.	Rém—2	500—505	Fine silty clay, shell-like fractured	39,9	0,18	8,0		

Table VI

Number	Boring: Locality	Boring: Depth m	Type of sediment	$CaCO_3$ %	Total salt %	pH (H_2O)	Age	
1.	Érsekcsanád—1	30—35	Fine sandy loess, light yellow	30,9	0,00	7,9	PLEI-STOCENE	
2.	Rém—1	57—62	Fine sandy small sand, yellow	15,5	0,00	8,0		
3.	Tompa—7	50,5—57,0	Fine silty loess, gray	18,9	0,00	8,4		
4.	Pusztamérges—2	55—56	Loess, humous, gray	22,1	0,03	7,8		
5.	Pusztamérges—2	100—100,5	Small sand, light gray, chalky	28,8	0,00	7,8		
6.	Érsekcsanád—1	95—100	Fine silt, light gray	4,4	0,00	7,8	PLIOCENE	LEVANTINE
7.	Rém—2	150—155/a	Fine silty, fine sandy coarse silt, light gray	15,5	0,00	7,9		
8.	Rém—2	150—150/b	Smaall sand and fine sand light gray	15,5	0,00	7,9		
9.	Jánoshalma—7	200—204,5	Clayey, coarse silty fine silt, dark gray, considerably humous	17,7	0,08	8,0		
10.	Pusztamérges—2	148—153	Coarse silty fine silt, light greenish-gray	19,9	0,03	7,9		
11.	Pusztamérges—5	250—255,5/a	Fine silt, light bluish-gray	15,5	0,05	9,4		
12.	Pusztamérges—5	250—255,5/b	Fine silt spotted humous	15,5	0,04	9,4		
13.	Üllés—1	280—286/a	Clayey fine silt, light gray, with mollusc rests	14,2	0,04	8,0		
14.	Üllés—1	280—286/b	Clayey fine silt, light yellow, calcareous spotted	9,7	0,03	8,0		
15.	Üllés—1	350—356	Fine sandy coarse cilt, light gray	15,0	0,02	8,5		
16.	Üllés—1	556—562	Coarse sandy fine silt, gray with brown dots	21,0	0,08	9,0		
17.	Üllés—1	718—723/a	Fine silty coarse silt, kight gray	20,8	0,10	8,8		
18.	Üllés—1	718—723/b	Clayey fine silt, light gray	25,2	0,08	8,9		
19.	Üllés—2	563—568	Clayey fine silt, light gray	20,2	0,07	9,0		
20.	Dunaújváros—1	103—105/a	Fine sandy clay, brownish-gray, with plant rests	0,00	0,00	8,2	PLIOCENE	UPPER PANNONIAN
21.	Dunaújváros—1	103—105/b	Silty fine sand, yellow, with limonitic stripes	20,8	0,00	8,0		
22.	Dunaújváros—1	152—154	Clayey fine silt, light gray	31,0	0,00	8,1		
23.	Dunaújváros—1	200,5—202,5	Coarse silty fine silt, light gray	35,4	0,03	8,1		
24.	Dunaújváros—1	251—253	Clay, iron-stainy light gray	22,1	0,00	8,1		
25.	Dunaújváros—1	302—304	Fine silty coarse silt, light gray	34,1	0,00	8,5		
26.	Dunaújváros—1	351—353	Fine silt, light gray	26,6	0,00	8,3		
27.	Dunaújváros—1	451—453	Small sand, partly fine frained and medium grained	17,7	0,00	8,3		
28.	Dunaújváros—1	500—502/a	Fine sandy small sand, light gray	17,7	0,00	8,5		
29.	Dunaújváros—1	500—502/b	Fine silt, small sand and fine sand, light gray	17,7	0,00	8,5		
30.	Dunaújváros—1	551—553/a	Coarse silty fine silt, light gray	18,6	0,08	8,2		

is higher than that of the Upper Pannonian. Analogous conditions in the rest of the Hungarian Basin are only known to the E, near Battonya (Fig. 1). In the NE of the Basin, region of Kemecse—Macs, the carbonate content is markedly lower (averaging some 5—6%) [B. MOLNÁR, 1966 *b, c, d*].

The carbonate content of the *Upper Pliocene* („Levantine" formation) varies between 4 and 25% (Table VI, samples N^{os} 6—19), averaging 16—17%. Thus some additional decrease is observed.

In the *Pleistocene* aeolian formation (Table VI, samples N^{os} 1—5) the amount of $CaCO_3$ is higher again from 20 to 25% [B. MOLNÁR, 1961, 1966*e, f*].

DETERMINATION OF THE TOTAL AMOUNT OF SALTS SOLUBLE IN WATER

The method is based on the electric conductivity of the soil as found for given conditions of humidity. The higher the concentration of soluble salts (electrolytes) in the sediment the lower its resistivity, i. e. the higher its electric conductivity [R. BALLENEGGER—J. DI GLERIA 1962].

In addition, conductivity is dependent on temperature; for this reason, to obtain values suitable for comparison, the resistivity values measured have to be converted with reference to so-called normal temperature (15.5°C). To facilitate this work, such an instrument has been used as shows automatically the percentage concentration of total salts in the soil sample [D. MUSZKA, 1959]. Thus the readings obtained represent corrected values already.

The method is suited to routine work but it yields only relative values of informative character.

For the analysis, a sample of 17,5 g weight diluted in 46,2 cm^3 of distilled water was stirred and then kept for 24 hours. Diagenized samples were first ground and then analysed.

The serial analyses under consideration, serving primarily to investigate saline soils, were carried out for experiment. For, it was supposed that the one-time inland sea had undergone additional freshening in the Pannonian and that this fact might be reflected by corresponding changes in the salt content of the sediments. Some information on the chemical composition of waters from aquifers of different ages in Hungary is already available. Accordingly, younger subsurface waters are less saline [K. KORIM, 1955; G. SZUROVY, 1957; Ö. SCHULHOF, 1957]. The question may arise how much does the original salt content change at the current technology of boring with flushing mud treated by various reagents, bearing in mind that the warm flushing mud may leach planty of substances from a core sample while reaching the surface.

In the more northerly part of the region the total percentage of water-soluble salts in the *Lower Pannonian* sediments cut by boreholes at Dunaújváros, Kecskemét, and Soltvadkert varied between 0.0 and 0.2% (Table II, samples N^{os}120—129). The highest value, 0.20, was obtained for a sample from Lajosmizse (sample N^{o} 122). For the rest, the salt content observed ranged, as a rule, from 0.11 to 0.12%.

For the S of the region, between Érsekcsanád and Pusztamérges (Table II, samples N^{os} 130—144), similar average values were obtained, though one sample gave a value as high as 0.22% (Table II, sample N^{o} 135). Samples from Üllés and Szeged, area East of the Pusztamérges Fault, already show a lower salt content,

averaging as low as 0.06—0.07% (Tables II—III, samples Nos 87—145). Sands or sandstones near Szeged are more common than in the areas hitherto discussed. Nor these are salty. Comparatively high salt content (0,50%) was, however, found in a sample from a humic bed lying at 1,490 m depth at Szeged (Table III, sample No 115).

It can thus be concluded that the Lower Pannonian sediments overlying a higher-seated basement in the W of the region have a higher salt content, whereas those lying above deep-sunken basement portions in the E are less saline. Carbonate-bearing and humic sediments sometimes yield conspicuously high values, while sands and sandstones do usually contain no water-soluble salt. In the latter case, salt is likely to have been dissolved by flushing mud.

In contrast with 0.14% obtained for the Lower Pannonian, the percentage of water-soluble salts in the *Upper Pannonian* formation at Dunaújváros has dropped to a few hundredths per cent. Many samples other than sand also lack salt. Irrespectively, the salt content was, as a rule, found to decrease upwards in the geological section (Tables V—VI, samples Nos 36—42). The Upper Pannonian samples from the borehole of Lajosmizse show rather a high salt content — 0.15 on the average (Table V, samples Nos 36—42). The Kecskemét and Soltvadkert samples have shown an upward decrease in salinity, the same holds true for the Upper Pannonian sediments of the Érsekcsanád—Pusztamérges area.

In the Upper Pannonian of the Üllés and Szeged areas, no marked change compared to Lower Pannonian has been observed, except for a slight increase of salt percentage in the lower part of the Upper Pannonian of drilling Üllés—1 (Tables III—IV, samples Nos 72—102).

The salt content of the *Upper Pliocene* („Levantine") sediments is low, from 0.9 to 0.1%, the average values being even lower: 0.04—0.05% (Table VI, samples Nos 6—19). Of the *Pleistocene* samples alone the loess of Pusztamérges was found to contain 0.03% of salt (Table VI, samples Nos 1—5).

Thus, it may be concluded that in the western part of the region, the salinity of the Lower Pannonian sediments is higher, showing a gradual decrease eastwards. The salinity of the Upper Pannonian sediments shows lower values for all the western area but the drilling at Lajosmizse, while in the surroundings of Üllés and Szeged no marked change occurs. The Levantine sediments, and particularly the Pleistocene ones, are of very low salinity, if at all. In assessing water-soluble salt content, particular attention must be paid to sands and sandstones of high humus and carbonate content and of high porosity.

In conclusion, the method under consideration seems to be suitable as a complementary one to other kinds of investigations for distinguishing sediments of different ages within a smaller area. Its further application, however, requires a large-scale additional experiment series.

pH MEASUREMENTS

The measurements to be discussed here were performed by using an electric pH-meter. 12,5 g of bore sample was diluted in 31,2 cm^3 of distilled water. The measurement was performed having kept the sample for 24 hours. Diagenized materials were previously subjected to grinding.

The *Lower Pannonian* sediments have rather a higher pH value (from 8.8 to 9.4%, averaging about 9.0; Table II, samples Nos 120—129) in the N of the region

(between Dunaújváros and Soltvadkert). In the S marked fluctuations could be observed (7.7—9.3) but its average was lower (8.6—8.7). Particularly low pH (with an average of 7.8) were obtained for bore-samples from Rém, remarkable for high carbonate and salt contents (Table II, samples N^{os} 131—134).

In the Üllés and Szeged areas the value of pH is rather high (between 8.6 and 9.4), averaging 8.8—9.0. Of course, the same samples show rather low carbonate and salt contents (Tables I—II, samples 145—169).

In terms of pH, the Lower Pannonian formation of the Danube—Tisza Interstream Region can thus be split up into two zones — that of Dunaújváros—Soltvadkert— Üllés—Szeged conspicuous for higher pH and that of Érsekcsanád—Pusztamérges showing lower pH.

The pH values (like the amount of soluble salts) of the *Upper Pannonian* of Dunaujváros show an upward decrease (still 9.1 at the base of the Lower Pannonian, they drop gradually, through 9.0—8.9—8.3—8.2, to a minimum of 8.0).

At Lajosmizse, where the total salt hardly changes from Lower toward Upper Pannonian, no change of the pH has been observed either. At Kecskemét and Soltvadkert, however, a slight decrease of pH was observed.

In the SW of the Region the low pH of the Lower Pannonian showed an additional decrease in the Upper Pannonian (7.6—9.4, with a marked frequency of values lower than 8.0; Tables IV—V, samples N^{os} 54—71).

In the *Upper Pannonian* of the Üllés and Szeged areas the value of pH varies within the range of 4.5—9.4, its average being higher than farther W (Tables II—IV, samples N^{os} 72—119). The value 4.5 and the two 8.0 readings were respectively yielded by a humic, pyrite-bearing sediment and by one slightly acid due to alteration of the former (Table III, sample N^{o} 115; Table IV, samples N^{os} 72—81).

The areal distribution of the pH values of the *Upper Pliocene* (Levantine) is similar to that found the Upper Pannonian, while the pH of the *Pleistocene* formation varies between 7.8 and 8.4.

The pH values can be applied only within areas of smaller geographic units. For, as shown by the measurements under consideration, those of the Lower Pannonian are high in the N of the Danube—Tisza Interstream Region, but very low in the SW.

The value of pH of the Upper Pannonian sediments of the N area (except for Lajosmizse) decreases from bottom to top, remaining, however, higher than in the SW. In the Szeged Basin it shows marked fluctuations, though its average is higher than farther W.

CONCLUSIONS

1. The average $CaCO_3$ content of the Lower Pannonian sediments of the Danube—Tisza Interstream Region was found to vary largely in the N, to be higher in the SW, lower in the Szeged Basin, yet mostly exceeds that of the average of the Upper Pannonian.

The lower carbonate content of the Upper Pannonian seems to be connected with the more variable sedimentation as well as the transgression of the Upper Pannonian inland sea resulting that only smaller areas of Mts. Mecsek and Mts. Villány with carbonate sediments remained emerged from the inland sea. So, the amount of $CaCO_3$ transported from these sources into the Upper Pannonian sedimentary basin was reduced.

2. The amount of the total water-soluble salts of the Lower Pannonian formations is greater in the western part of the region, whereas it decreases toward E. The total salt content decreases in the western part of the region in the Upper Pannonian layers — except the bore-hole at Lajosmizse — whereas it does not change substantially in the area of Szeged Basin. The Upper Pliocene sediments especially the Pleistocene ones, show low salinity, if any. Added to other kinds of investigations, the present method can be used for distinguishing formations of different ages within a smaller areal unit.

3. The pH of the Lower Pannonian is high in the N of the region and in the Szeged area, being lower in the SW. That of the Upper Pannonian shows an upward decrease all over the N but Lajosmizse, yet it remains higher than was found for the SW area. In the Szeged Basin it shows marked fluctuations, though its average is higher than farther W.

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EXAMINATION OF CEMENT—INDUSTRY RAW MATERIALS FROM THE SW BÜKK MOUNTAINS

by

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Our Institute carried out, in the years 1964—1965, a limestone and clay exploration, for the planned cement plant in the neighbourhood of Eger—Felnémet. For limestone prospecting, the limestone and marl strata composing the Bükkbérc-range, for the purpose of clay the Middle-Oligocene stratas between Eger and Noszvaj seemed the best suited *(Fig.* 1). The manysided investigation of materials of 11 borings (1514 meters) from the Bükkbérc and that of 34 borings (1210 meters) in the neighbourhood of Noszvaj were carried out.

GEOLOGICAL CONDITIONS OF THE AREA

The geological structure of the exploration area is demonstrated on *Fig.* 1. In accordance with this, first Eocene terrestrial, later marine formations are deposited upon the Triassic.

We tried to penetrate, with the 300 meter deep Bikkbérc № III—0 drilling, the Eocene terrestrial strata too, drilled earlier with 257 meter thickness in the bore-hole Noszvaj (Sikkut) № 1. The well bored in 179,5 meter thickness, from 120,5 meter to the bottom, consists of mostly many-coloured sandy clay layers. Thin sandstone, sand, gravel and clayey breccia interbeddings are in the many-coloured clay. Ladine age shale, gravel of sandstone origin and again many-coloured clay followed in between 287—290 meters. The „gravel" supposedly means that the bot tom of terrestrial stratas is near. For the time being, the age of terrestrial stratas is not cleared reassuredly since pollens or other fossils are missing.

All the wells of Bikkbérc reached the average 1—2 meter thick lowest part of the Upper-Eocene marine strata, composed from base conglomerate, with clayey-marly binding material, and breccia. First clayey marl, marl, calcareous marl, afterwards clayey limestone and limestone is bedded upon the base conglomerate.

We found thinner limestone stratas too, in the marl-calcareous marl deposits, which compose a quarter part of the marine layers, penetrated with 72 to 177 m thickness in the wells. But the bulk of the clayey limestone and limestone was found in the upper 3/4 of the sequence of layers. The bedding of stratas is shown in *Fig.* 2.

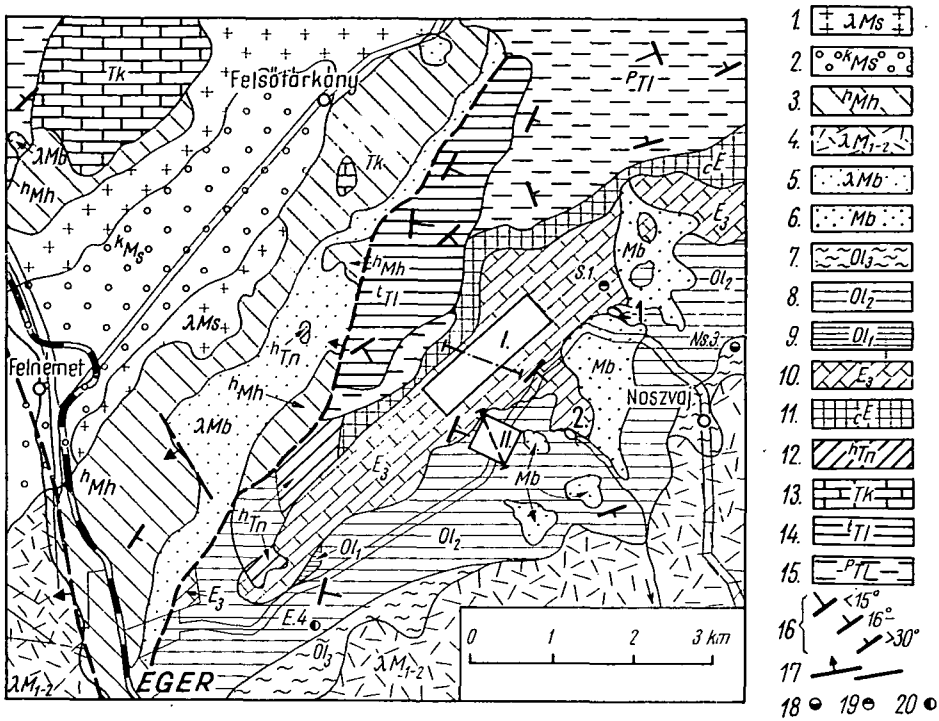

Fig. 1. Geological sketching map of the surroundings of Eger—Felsőtárkány—Noszvaj. (after K. BALOGH) *1. Sarmatian* upper rhyolite tuff; *2.* gravel, sand, terrestrial clay, partly with tuff; *3. Helvetian* clay, sand, sandstone, gravel, brown coal; *4.* rhyolite tuff; *5.* lower rhyolite tuff, gravel and lower rhyolite tuff; *6. Burdigalian* gravel, sand, sandstone, conglomerate, coloured clay and gravel; *7. Kattian* sandy clayey marl: *8. Rupelian* grey clay and clayey marl with sandstone and andesite tuff layers; *9. Lattorfian* grey clay and calcareous marl; *10. Bartonian* lithothamnium and nummulitic limestone and calcareous marl; *11. Lower Eocene* terrestrial many-coloured clay, sand, gravel; *12. Norian* grey limestone; *13. Karn* „berva limestone" *14.* grey chert limestone partly with dolomite; *15. Ladine* dark grey shales, sandstone with chert limestone or siliceous shale interbeddings; *16.* Dip; *17.* Fault; *18.* oil exploration well; *19.* brown coal exploration well; *20.* manganese exploration well; I. Limestone exploration area; II. Clay exploreation area. 1. Sikfőkút; 2. Forrókut.

In the marine formations the *Nummulites fabianii* Prever is frequent, as well in limestone as in marls. This and the *Neocarpenteria cubana* [CUSHMAN and BERMUNDEZ], *Stomatorbina torrei* [CUSHMAN and BERMUNDEZ], *Queraltina epistominoides* MARIE, *Chapmanina gassinensis* [SILVESTRI], *Spirolypeus granulosus* [BOUSSAC], *S. carpaticus* [UHLIG], *Grzybowskia multifida* BIEDA, *G. reticulata* [RÜTIMEYER] found in the same complex, gives the age of Upper Eocene.

In the Middle Oligocene stratas of the Noszvaj clay exploration area, tested generally with 40 meter deep wells, the brown, yellow and grey coloured, mainly silty clay, clayey silt, rock floured silt, silty rock flour, less sandy rock flour, rock floured sand and sand, rarely sandstone stratas are alternating with one another. Some layers of these are more hard and compact.

The foraminifera species determined by Mrs. MARIA JÁMBOR from the samples of well № I—3 and I—9 for justifying the age of the formations represent the foraminifera horizon № 3 (agglutinated) according to MAJZON.

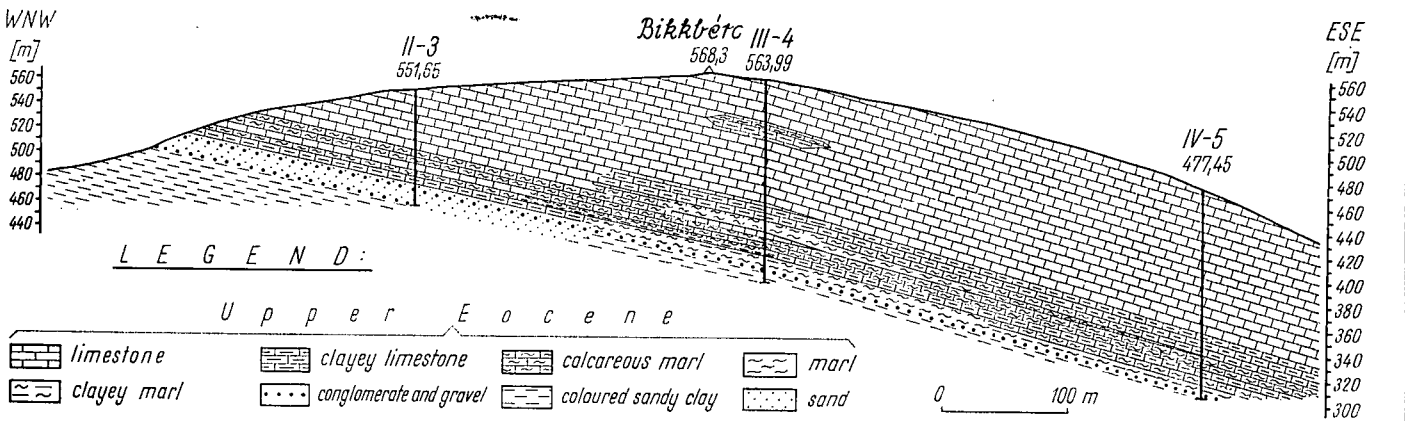

Fig. 2. Geological profile of the Bikkbérc limestone exploration area.

The Middle Oligocene formation discovered by drillings, contains generally 2, 3 or 4, averagely 2,39 meter thick little manganic and 1,81 meter thick manganic silty rock flour, rock floured silt, clayey silt and silty clay stratas. It is known on the base of manganese ore explorations made earlier in the neighbourhood, that the scattered found manganic clay layers are not commercial deposits for the manganese mining. The manganese ore exploring well Eger № 4, transversed the Middle Oligocene clay-clayey marl formations till the depth of 114,4 meters. This formation is several hundred meters thick, on the base of drilling datas from the greater region.

2—8 m thick reddish brown, brown silty clay, clayey silt and rockfloured silt, Pleistocene cap rock is bedded upon the Middle Oligocene stratas.

On the maps and sections, the silty clay, clayey silt and rock floured silt layers, important resources used for cement fabrication, are summed up as stratas of clayey development.

For the qualitative presentation of rock materials, SM (silicate module) maps and profiles were constructed. The drawing of the boundaries of quality were coordinated with the geologic sections from the same place, *(Fig.* 3) during completing of SM profiles. These illustrate first of all the industrial utilization of the raw material and in the same time the petrographical conditions of the area.

The faulted forms are characteristic of the structure of the Bikkbérc and Noszvaj exploration areas.

The Upper Eocene stratas of Bikkbérc, risen along NNE—SSW (generally 30°—210°) faults, dip in ESE direction (120°) averagely with 15° *(Figs.* 2 *and* 3*a)*.

Further, small faults are probable on base of morphological conditions in the limestone formations of Bikkbérc.

In the geological dip profile of the Middle Oligocene area bordered also by NNE—SSW faults *(Fig.* 3*a)*, the stratas have a 12—15° dip, with ESE direction.

The slightly manganic lenses prospected by drillings, were well usable the identification of stratas in contradiction to the case of experiences from the region of Eger.

Hydrogeology. The setting of the ground-water in the Noszvaj clay exploration area, is shown with the static ground-water level datas of the subsoil map and geological sections *(Fig.* 3*a)*. Where the water level data is not shown, there was no ground- nor layer-water observed till the bottom of the drilling.

The karstic features of the limestone — calcareous marl layers of the exploration area of Bikkbérc were shown by the escape of the drilling fluids as well as by the caverns detected by geophysical methods. Comparing the places of the water-escape — which amounts to 5—32 m^3 per shift — and the locations of the fissures and the caves to be supposed on the basis of sharp peaks of the gamma — gamma and neutron — gamma curves, in many cases a good agreement could be established.

The Middle Oligocene clay — clayey marl is generally impermeable for water and plays a damming role on the margin of the mountains. The Upper Eocene nummulitic limestone and calcareous marl is theoretically a good water reservoir. Its water-houshold is common with the Middle Triassic limestone. Water was yet not observed in the exploration wells of the Bikkbérc area, because they penetrated only the downward karst. The wells of Sikfőkut, flowing from Upper Eocene nummulitic limestones in 340 m and the Forrókut wells in 280 m highness above sea level as structural wells too, indicate the supposed karst water-level banked up by Middle Eocene clay formations *(Fig.* 1*)*.

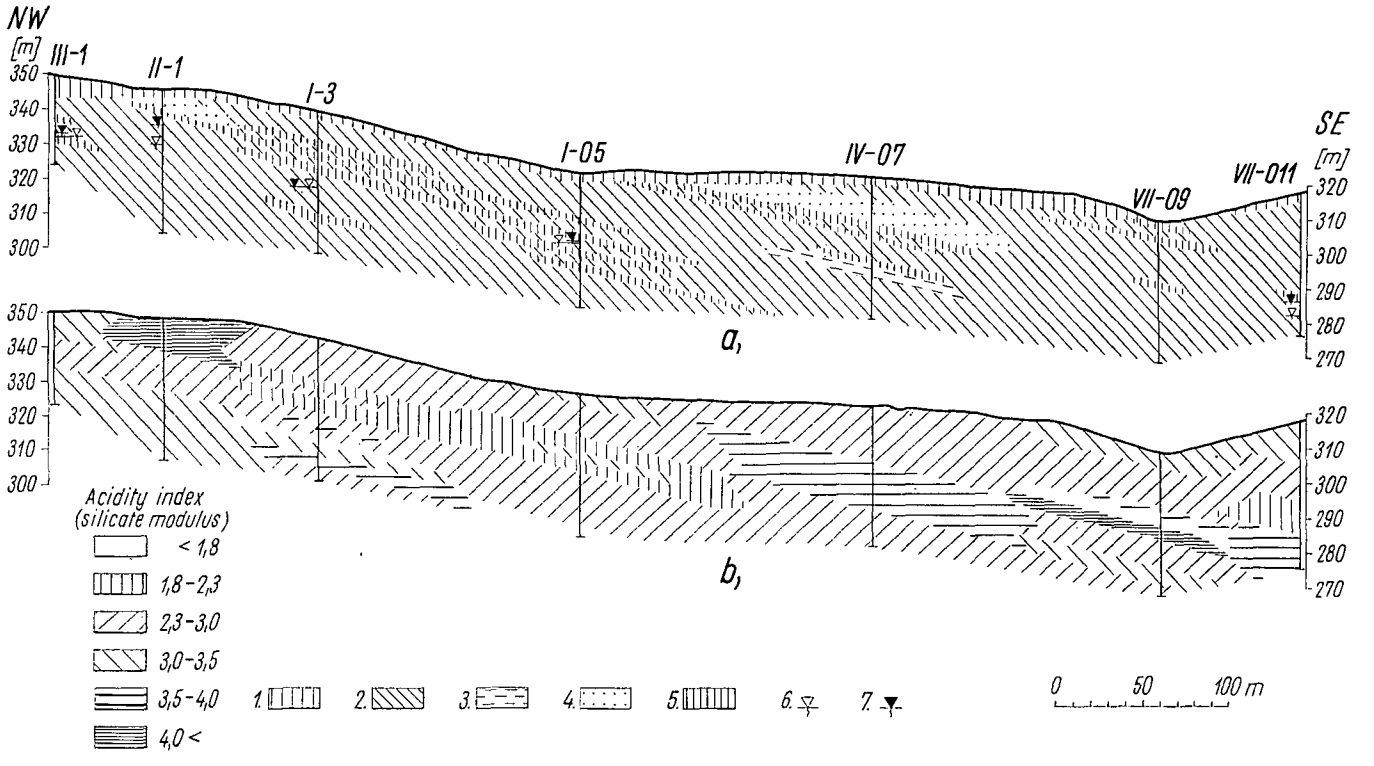

Fig. 3. Geological profile of the Eger—Noszvaj clay exploration area (s), and SM profile (b). *1. Pleistocene* rock floured silt, clayey silt, silty clay; *2. Middle Oligocene* rock floured silt, clayey silt, silty clay; *3.* silty rock flour; *4.* fine sandy rock flour, sandy rock flour, rock floured sand, sand; *5.* silty rock flour with manganese patches and manganese, rock floured silt, clayey silt, silty clay; *6. ground*-water level; *7.* static ground-water level.

Average and extreme values of chemical analyses* Table 1.

	Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	MnO	SO_3
	Weight percent										
Limestone (U-E)**											
Average	42,40	1,70	0,60	0,36	0,04	34,12	0,22	0,42	0,41	—	0,30
Minimum	39,05	0,25	0,10	0,14	0,02	50,37	0,03	0,07	0,11	—	0,03
Maximum	44,08	3,50	2,47	0,79	0,05	55,69	0,83	0,96	1,67	—	1,37
Clayey limestone (U—E)											
Average	40,20	6,84	2,34	0,81	0,10	49,28	0,32	0,36	0,44	—	0,84
Minimum	38,28	1,55	1,34	0,12	0,10	46,37	0,04	0,08	0,12	—	0,01
Maximum	42,42	9,07	3,81	1,55	0,15	51,09	0,80	0,85	0,87	—	2,02
Calcareous marl (U—E)											
Average	31,29	20,11	6,24	2,04	0,35	36,19	1,38	0,20	0,65	0,55	2,27
Minimum	30,71	17,34	4,84	1,62	0,29	35,74	0,19	0,08	0,45	0,55	0,75
Maximum	32,03	24,15	7,82	2,35	0,40	36,73	3,83	0,39	0,94	0,55	3,12
Marl (U—E)											
Average	24,83	31,05	8,48	3,13	0,44	27,20	1,01	0,26	0,48	—	3,40
Minimum	21,31	25,41	4,07	2,47	0,22	20,55	0,34	0,08	0,09	—	1,50
Maximum	27,97	34,22	13,70	3,89	0,57	31,14	1,98	0,73	0,90	—	6,30
Many-coloured sandy clay (U—E)											
Average	5,27	59,47	16,72	5,30	0,23	0,59	0,39	0,34	1,31	—	0,10
Minimum	4,08	55,52	13,61	1,56	0,16	0,18	0,04	0,07	0,23	—	0,02
Maximum	8,34	74,29	19,67	9,95	0,31	1,31	0,89	0,81	2,07	—	0,45
Rock floured silt — silty clay (Ol)											
Average	11,30	51,30	11,91	5,54	0,62	8,42	2,91	0,84	2,03	3,65	1,74
Minimum	6,17	22,84	0,45	3,37	0,15	1,40	0,21	0,23	0,71	0,12	0,14
Maximum	22,18	66,39	16,49	9,36	0,88	18,45	9,79	1,87	3,27	22,67	5,40
Rock floured silty clay — silty clay (Pl)											
Average	9,82	55,90	14,29	7,23	0,84	4,15	1,24	0,44	1,54	1,75	0,81
Minimum	8,09	52,29	12,62	6,03	0,74	1,84	0,15	0,22	1,29	1,60	0,81
Maximum	12,40	64,25	16,49	7,99	0,90	8,38	1,97	0,74	1,98	1,91	0,81

* Remarks: Maximum and minimum values in the Table, are not everywhere datas of the same rock samples.

** (U—E)= Upper Eocene, (Ol)= Middle Oligocene, (Pl)= Pleistocene

QUALIFYING TEST OF RAW MATERIAL

The rock material explored by borings, was first of all tested to decide the appropriateness for cement industry and for the mineralogical- petrographical knowledge of the area.

Chemical investigations. From the Bikkbérc limestone explorating area, altogether 298 (56 total and 242 partial) analyses were carried out. During the partial chemical analyses the $CaCO_3$, CaO and MgO contents of rocks were determined. We used BÁRDOSSY's nomenclature for defining sorts of limestones. The average and extreme values of the total analyses are shown in Table 1.

We made a total of 191 (44 total and 147 partial) chemical analyses from the Noszvaj clay exploration area (Table 1). From the 44 analysed samples, the MnO content of 7 samples varies between 6,84—22,58 per cent. We found in 30 other samples smaller quantities of (average 0,76 per cent) MnO. The above results are in accordance with the data of the published literature from the area.

For technological evaluation and estimating of reserves the SM values of the raw material were calculated. The average and the weighted SM value of the useful material is equally 2,85.

Thermal examinations. To ascertain the mineral composition of samples, thermal (derivatographic and dilatometric) examinations were carried out. The thermograms of 5 characteristic samples of 100 thermograms of the two exploration areas, are shown in *Figs.* 4—8.

On the thermogram of the Upper Eocene limestone only the endothermic peak characteristic of calcite can be observed, other peaks pointing to the presence of other crystalline phases do not appear *(Fig.*4). The DTA curve of *Fig.* 5 (Upper Eocene marl) shows an exothermic peak between 200—400°C characteristic of

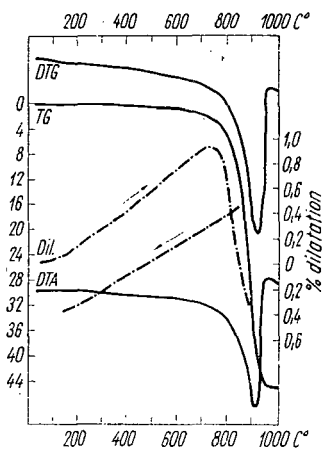

Fig. 4

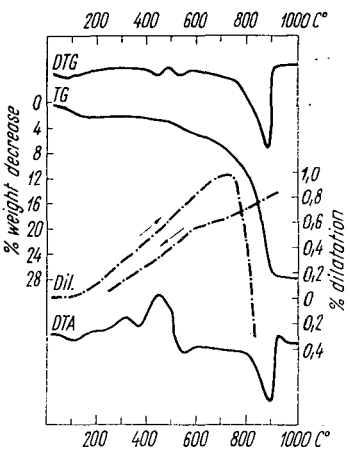

Fig. 5

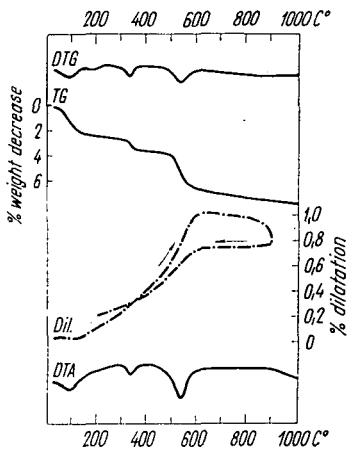

Fig. 6

Fig. 4. Thermal curves of the Upper-Eocene white limestone, from 15,0 m depth, No IV-5 boring Bikkbérc.

Fig. 5. Thermal curves of the Upper-Eocene grey marl, from 71,8—72,3 m depth. No IV. 3. boring Bikkbérc.

Fig. 6. Thermal curves of the Upper-Eocene many-coloured sandy clay, from 240,8 m depth, No III-0 boring Bikkbérc.

organic materials. The dilatation curves indicate quartz impurities of the limestones. The cooling curves show *(Fig.* 5 for example*)* a small quantity of quartz.

According to the thermograms of many-coloured sandy clays from the borehole Bikkbérc N III—0, the terrestrial stratas on the base of Upper Eocene, are mineralogically fairly uniform. The dilatation curves are characteristic of illite and quartz. We observe hereby that the average SM values of the mainly many-coloured sandy clay formations is 3,42, the extreme values are 2,35—5,10 *(Fig.* 6*)*.

The thermogram typical for the Noszvaj Middle Oligocene clay area is shown on *Fig.* 7. The sample contains illite and montmorillonite according to the DTG, DTA and dilatation curves. The montmorillonite character is dominant especially

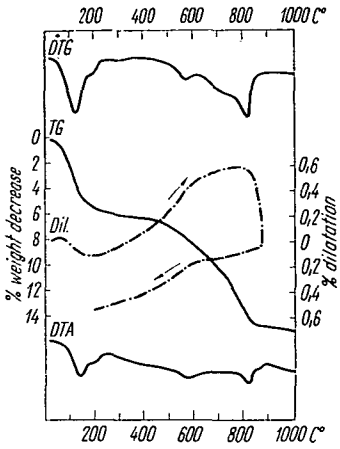

Fig. 7

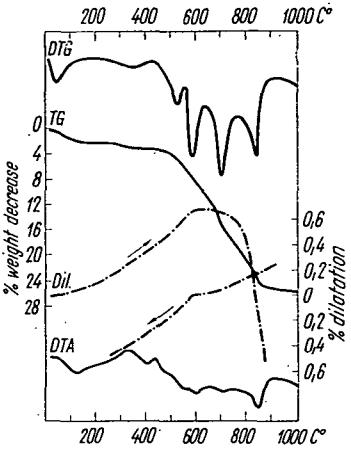

Fig. 8

Fig. 7. Thermal curves of the Middle Oligocene greyish silty clay, from 14,0 m depth, No I-9 boring, Eger—Noszvaj.

Fig. 8. Thermal curves of the Middle Oligocene grey (manganic) rock floured clayey silt, from 29,0 m depth, No I-3 boring, Eger—Noszvaj.

on the dilatation curves of the quartz-poor materials. The manganese carbonate, characteristic of materials with higher Mn content, is rodochrosite on the DTG curves *(Fig.* 8*)*. In the DTA curves of samples with higher iron content, a peak characteristic of pyrite is to be seen. Besides this, peaks for calcite or dolomitic calcite are important.

X-ray examinations. After the evidence of 73 X-ray diffractograms, part of the limestone and marl samples of Bikkbérc are contaminated with quartz. Kaolinite could also be determined in the clayey limestone. This was not possible on the thermograms because of its poorly crystallization.

In the many-coloured clay formations, bored in well № III—0, hematite is present too, below 250 m depth. Clay minerals of this formation tested with X-ray examinations, are illite and kaolinite.

The results of the X-ray investigations from the Noszvaj exploration area, are in good agreement with that of the thermal investigations. A small quantity of kaolinite could be determined in many samples. This is not present with pointed peaks on the derivatograms. Feldspars are to be found subordinately in a great part of the samples.

We made grain size distribution examinations, to define better the characteristic materials of the Noszvaj exploration. We measured the grain-size distribution of samples, which belong to the normal or peptized (without coagulation)

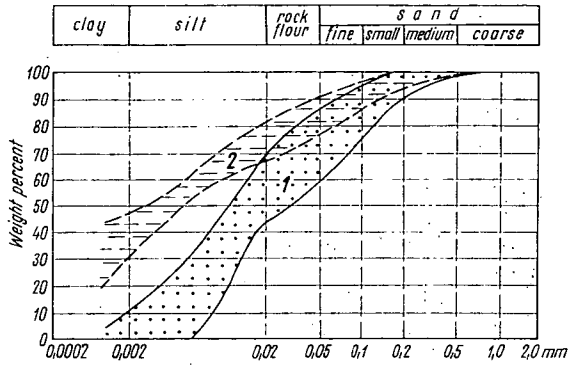

Fig. 9. Grain size composition cover curves of the investigated Middle Oligocene stratas from the clay exploration area of Eger—Noszvaj. *1.* Normal state; *2.* Peptized state.

state. The peptization was made with sodium ion exchange. The cover curves of grain size composition, on *Fig.* 9, show the extreme values in normal and peptized state. In accordance with this, the weight per cent of the clay fractions ($<0{,}002$ mm) changes between 0—10,5 in normal state and between 32,5—48,0 in peptized state. The flat curves reaching several ranges, illustrate the bad sorting of the sediments.

SUMMARY

The detailed geological knowledge of the two exploration areas, further the qualifying tests of materials, succeeded in the preliminary exploration of the planned cement plant's limestone and clay material. The limestone is directly accessible on the surface. According to the investigations, within the Upper Eocene formation every transition from the marl to the limestone can be found. Great part of the tested samples contains organic materials indicated also by thermal methods. In the limestone-marl stratas partly thin clay of marine origin partly clayey interbeddings formed afterwards during the weathering were found. The limestone has an average $CaCO_3$ content of 94,6 per cent, the clayley limestone 85,5 per cent, the calcareous marl 70,5 per cent and the marl 49,0 per cent. Below these layers mostly Upper Eocene terrestrial many-coloured clay stratas are deposited containing illite, kaolinite and quartz and in the deeper layers hematite too.

The clay of Middle Eocene age is to be found also on the surface. But its utilization is difficult owing to the interbedded manganic and sandy layers. The raw material contains dominantly illite, montmorillonite and less kaolinite.

The clay minerals are of divalent cation base, strongly coagulated. About 92 per cent of the samples investigated is of limy character, the carbonates are mostly present (6—20 per cent) as calcite and dolomitic calcite, respectively, according to the thermal and X-ray examinations.

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CONTENTS

Correlation between electrostatic energies and energy contants of some complex oxyanions. *Gy. Grasselly* 3

Pleistozäne Deflationserscheinungen in südwestlischen Teil des Mecsek-Gebirges. *Á. Jámbor* 13

Contribution to the knowledge of the magnetite-hematite system of oxyvolcanites. *J. Mezősi* 23

Lithological and geological study of the Pliocene formations in the Danube-Tisza interstream region. Part II. *B. Molnár* 35

Examination of cement-industry raw materials from the SW Bükk Mountains. *Gy. Vitális* and *J. Hegyi-Pakó* 47

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